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Field Measurement of Denitrification

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16. ABSTRACT

Denitrification from a Yolo loam field profile was studied in relation to the influence of soil-water content, organic carbon source, and temperature. Field plots were intensely instrumented with soil atmosphere samplers, soil solution samplers, and tensiometers. The two soil-water pressure treatments were -0.01 and -0.05 bars in the topsoil. Three levels of soil carbon were studied by evaluating plots cropped with ryegrass, uncropped plots, and plots amended with manure. Experiments were conducted at soil temperatures of 8 and 23°C. Fertilizer was applied as KNO_3 enriched with ^{15}N. The flux of volatile gases at the soil surface was measured from the accumulation of N_2O and $^{15}N_2$ beneath an air-tight cover placed over the soil surface for 1 or 2 hours per day. Denitrification at 23°C ranged from 73% of the fertilizer N for the manure treatment at -0.01 bar to 1% for the uncropped treatment at -0.05 bar. At 8°C, denitrification ranged from 11% for the manure treatment at -0.01 bar to zero for the uncropped plots. The N_2O flux at the soil surface varied between 5 and 26% of total denitrification.

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in groundwater; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American public.

William C Galegar

William C. Galegar
Director
Robert S. Kerr Environmental
Research Laboratory

ABSTRACT

The amount of NO_3^- in irrigation return flow waters is dependent upon each of the components of the N cycle in soils. One of those components for which absolute amounts and rates are not well known is denitrification. Volatile denitrification products, primarily N_2O and N_2, are evolved whenever anoxic sites develop within the soil and when sufficient carbon is available. Absolute amounts and rates of denitrification from a Yolo loam field profile at Davis, California, were studied in relation to the influence of soil-water content, organic carbon source, and soil temperature. Field plots were intensely instrumented with soil atmosphere samplers, soil solution samplers, and tensiometers. Soil-water pressure heads (h) in the upper 15 cm of soil were maintained constant at -15 and -70 cm of water and at -8 and -50 cm of water for the soil temperature treatments (5 cm depth) of 23 and 8°C, respectively. Plots cropped with ryegrass, uncropped plots, and plots to which manure was mixed in the top 10 cm of soil were used to establish three different carbon levels. Fertilizer was applied at the rate of 300 kg N ha^{-1} as KNO_3 enriched with 20 and 40% ^{15}N for the h = -15 or -8 and h = -70 or -50 cm treatments, respectively. The flux of volatile gases at the soil surface was measured from the accumulation of N_2O and $^{15}N_2$ beneath an air-tight cover placed over the soil surface for 1 or 2 hours per day and from measured soil gaseous diffusion coefficients and concentration gradients. Denitrification from gas fluxes occurred for the high-temperature experiment in order of decreasing magnitude in manure (h = -15 cm), manure (h = -70 cm), cropped (h = -15 cm), cropped (h = -70 cm), uncropped (h = -15 cm), and uncropped (h = -70 cm) plots. Approximately 70% of the fertilizer N was denitrified for the manure (h = -15 cm) treatment. Approximately 1% of the added fertilizer was denitrified in the uncropped (h = -70 cm) treatment. Denitrification from gas fluxes for the low-temperature experiment occurred in the same order as that of the high-temperature experiment except that the rate and absolute magnitude were much smaller. Approximately 11% of the fertilizer N was denitrified for the manure (h = -8 cm), and no measureable denitrification occurred in the uncropped (h = -50 cm) treatment. The amount of N_2 produced was much greater than N_2O. The N_2O flux at the soil surface varied between 5 and 26% of total denitrification.

Denitrification measured from gas fluxes compared reasonably with that determined by difference of all other components of the N cycle for the wettest water treatments. For the drier treatments, denitrification measured directly was smaller than that determined by difference due to the inability to measure very small fluxes of $^{15}N_2$ over relatively long time periods, inability to continuously monitor gas fluxes, and uncertainty in measuring denitrification by difference. Determining denitrification by difference was highly uncertain due primarily to variability of the water flux and NO_3^- concentrations within the soil.

Since nearly all denitrification occurred in the upper 30-60 cm of soil, the amount of NO_3^- leaching below the root zone was strongly dependent upon the soil-water treatment and the amount of carbon for denitrification. Nitrate was completely leached from the 180 cm profile after approximately 7 months in the h = -15 and -8 cm treatments, whereas nearly all NO_3^- remained in the upper 60 cm of soil for the h = -70 and -50 cm treatments.

The proportion of volatile products and rates of denitrification as influenced by field-soil environmental conditions can only be ascertained by measuring the flux of the gases produced. A thorough, quantitative evaluation of the rate and magnitude of denitrification, leaching, and plant uptake provides a means for making management decisions to control irrigation return flow water quality.

This report was submitted in fulfillment of Grant No. R-804259 by University of California, Davis, under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from December 1, 1975, to July 31, 1977, and work was completed as of August 8, 1977.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

cm	-- centimeter
m	-- meter
ml	-- milliliter
^{o}C	-- degrees Centigrade
kg ha^{-1}	-- kilograms (10^{3} grams) per hectare
mg	-- milligram (10^{-3} grams)
ppm	-- parts per million on a weight basis
ppmv	-- parts per million on a volume basis
cm^{3}	-- cubic centimeters
g	-- gram
µg	-- micro grams (10^{-6} grams)

SYMBOLS

N	-- Nitrogen
NH_4^+	-- Ammonium
NO_2^-	-- Nitrite
NO_3^-	-- Nitrate
NH_3	-- Ammonia
N_2O	-- Nitrous Oxide gas
N_2	-- Nitrogen gas
^{15}N	-- Nitrogen isotope of mass 15
CO_2	-- Carbon dioxide gas
O_2	-- Oxygen gas
f	-- gas flux (mg cm^{-2} day^{-1})
D_p	-- soil gaseous diffusion coefficient (cm^2 day^{-1})
C	-- gas concentration (mg cm^{-3})
x	-- distance (cm)
h	-- soil-water pressure head (cm)

SYMBOLS (continued)

θ -- soil-water content ($cm^3\ cm^{-3}$)

ε -- soil-air content ($cm^3\ cm^{-3}$)

v_s -- soil-water velocity ($cm\ day^{-1}$)

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SECTION 1

INTRODUCTION

The amount of NO_3^- reaching the ground water of irrigated lands is dependent upon each of the components of the N cycle in soils. The amount of fertilizer N applied and crop uptake of N are easily measured parameters of the total balance. The other components of the N balance, however, are not as easily measured or determined. The leaching component of the N balance has been a subject of much study and is the primary concern in terms of NO_3^- in ground water. The natural spatial variability of the leaching component has been demonstrated to be large (Biggar and Nielsen, 1976). The other components such as residual soil N, denitrification, and NH_3 volatilization losses are also not easily measured. The residual soil N is difficult to measure due to the large organic N pool of most soils and complicated by the natural spatial variability of that pool (Rolston, 1977). The transient processes of immobilization and mineralization within the large organic N pool also contribute to the complexity of the measurement. Volatilization loss of fertilizer as NH_3 occurs to varying degrees in calcareous soils. This component can generally be minimized by incorporating NH_4^+ fertilizer below the soil surface. Another loss of N from the soil system for which absolute amounts and rates are not well known is denitrification. Volatile denitrification products, primarily N_2O and N_2, are evolved whenever anoxic sites develop within the soil and when sufficient carbon as supplied by soil organic matter, plant materials, and manure is available.

Simulation models of the N balance in soil systems attempt to predict the amount and concentration of NO_3^- in irrigation return flow water as a function of irrigation and cropping practices (Mehran and Tanji, 1974; Donigian and Crawford, 1976; Shaffer et al., 1976; Tanji and Gupta, 1977; and van Veen, 1977). In general, the denitrification component of the various mathematical models has not had adequate input data especially for the rates of denitrification. Total denitrification of applied fertilizer is used quite frequently such as 10-15% of the fertilizer N applied (Fried et al., 1976).

Very few experiments have evaluated the absolute amounts and rates of denitrification in the field. Rolston et al. (1976) demonstrated that the volatile gases from denitrification could be measured in a field profile. Total denitrification from gas fluxes compared reasonably with denitrification determined by difference for a small, intensely-instrumented, field plot. Total denitrification was determined by integrating with time the flux of the gaseous denitrification products as determined from measured soil gaseous diffusion coefficients and concentration gradients. However, these studies only evaluated the amount of denitrification under one cropping or carbon

input system and one soil-water content near saturation.

The objectives of the research reported here were:

a. To measure denitrification in a field soil directly from the fluxes of N_2 and N_2O at the soil surface.

b. To compare denitrification obtained from N_2 and N_2O gas fluxes with denitrification obtained by difference.

c. To measure the amount of denitrification from an applied inorganic fertilizer source as affected by an actively growing crop or manure amendment, soil-water content, and temperature of a field soil.

The research was conducted on small 1-m^2 field plots because of the large cost of NO_3^- fertilizer tagged with high enrichments of the stable isotope ^{15}N. The use of ^{15}N tagged NO_3^- is presently the only positive means of measuring N_2 gas resulting from denitrification in the field. The experiments were conducted at a high and low soil temperature, at two water contents near saturation, and at three levels of carbon input (cropped, uncropped, and manure).

SECTION 2

CONCLUSIONS

The results of this research demonstrate that denitrification can occur at very large rates with the largest rates occurring soon after application of NO_3^- fertilizer to soil maintained constantly wet. The rate of denitrification generally decreases rapidly after the initially large rate due to a decrease in NO_3^- concentration and to the movement of the NO_3^- pulse out of the zone of high carbon content and low oxygen concentrations. For soils in which the profile development is such that large bulk densities occur near the surface, denitrification is limited to the top 30 to 60 cm of the soil profile inasmuch as that is the zone where water content is greatest, soil-air content is smallest, and biological activity is greatest due to generally high carbon values. Thus, denitrification would be greatest in the surface zone. This is not an uncommon situation for many alluvial, irrigated soils of the West.

Denitrification occurs over a very narrow range of soil-water content on Yolo loam soil. Very little denitrification occurred in plots at which the soil-water pressure head was maintained at -70 cm of water. This soil-water pressure head corresponds to a soil-air content of 9-10%. It would be expected that for alluvial, loam soils such as Yolo, that very little denitrification would occur if soil-water pressures were maintained smaller than approximately -100 cm of water.

The presence of the crop root system has a large influence on denitrification. For the Yolo loam soil, very little denitrification occurred even at the water content nearest water saturation if a crop was not growing on the soil. The influence of the root system in providing carbon and consuming O_2 results in anoxic development and provides the carbon necessary for denitrification. As expected, the addition of manure to the soil greatly increased denitrification over that of the cropped plots. It would be expected that the addition of other organic materials such as crop residues along with the NO_3^- fertilizer would also have the effect of substantially increasing denitrification. With manure added to the soil and water contents maintained very close to saturation, approximately 73% of the fertilizer was lost by denitrification at 23°C. Only 14% of the fertilizer was lost in the cropped, wet treatment of the summer experiment. Only 3% of the NO_3^- was lost for the wet treatment of the summer experiment without a crop growing on the soil.

At a soil temperature of between 8 and 10°C, very little denitrification occurred. This was primarily due to limited microbial activity as reflected in relatively constant O_2 concentrations with soil depth. The largest denitrification loss at the low soil temperature occurred in the wet, manure treatment with 11% of the fertilizer denitrified. The uncropped plots lost

very little NO_3^- at the low soil temperatures.

The predominant gas evolved was N_2 with total amounts being at least 6 times greater than that for N_2O, and in some cases 20 times more N_2 than N_2O was produced under very anoxic conditions. The N_2 to N_2O ratios were generally small (1 to 5) early in the denitrification process and then became much larger as denitrification proceeded.

Measurement of denitrification from the gaseous components was slightly smaller than that measured by difference. This failure to account for the total amount of N apparently denitrified was most likely due to the inability to continuously monitor gas fluxes, to very small rates of denitrification over an extended time period after the initially large rates had decreased, and to errors in the difference method. The sensitivity of the instrumentation was not sufficient to measure denitrification rates less than approximately 1 kg N ha^{-1} day^{-1} over many days or weeks. Although denitrification measured from gas fluxes was less than that determined by difference due primarily to the lack of sensitivity in measuring small denitrification rates, measuring N_2 and N_2O is the only means that the rates and position of denitrification in the profile can be ascertained. The sensitivity for measuring small gas fluxes can be increased by increasing the ^{15}N enrichment of the added fertilizer and by increasing the time that covers are left in place at the risk of changing the normal soil condition.

Calculations of the denitrification gas flux from the soil gaseous diffusion coefficient and gas concentration gradients measured within the soil compared reasonably with measured fluxes of N_2 and N_2O as determined by taking gas samples from beneath the cover placed over the soil surface for 1- or 2-hour time intervals on each sampling day. This statement is valid only if the diffusion coefficient is measured immediately before and after an experiment is conducted, since the values of the diffusion coefficient were very much dependent upon surface soil conditions. Since $^{15}N_2$ concentrations within the soil were greater than those under a cover, increased sensitivity should be possible if concentration gradients and diffusion coefficients can be accurately measured.

All NO_3^- had been leached from the profile of the wet treatments by 7 months after application of the fertilizer. In the dry plots, most of the NO_3^- was still in the upper 60 cm of the soil profile after 5 months. Therefore, the amount of water applied and the soil-water velocity has an enormous effect on the amount of NO_3^- leaching and the position of the NO_3^- within the soil profile.

Determination of the leaching component was highly uncertain due to errors in determining the soil-water flux and variability in NO_3^- concentrations. For the low-temperature experiment, it was impossible to obtain a mass balance inasmuch as N leaching was greater than N applied as fertilizer. This discrepancy was attributed primarily to an overestimation of the soil-water flux resulting from spatial variability, flux changes with time, and anion exclusion or immobile water. Errors are also possible in measuring the residual soil N. Thus, the determination of denitrification by difference is highly uncertain.

Both cropped plots of the wet and dry treatments took up fertilizer N at approximately the same rate until the NO_3^- was either denitrified or leached from the upper part of the profile. The rate of uptake for the wet treatments decreased to near zero after the NO_3^- had been leached from the upper 60 to 90 cm of the profile, whereas uptake continued in the dry treatments where the NO_3^- was still in the upper portion of the profile and being taken up by the grass.

It would be expected that considerable fertilizer N would be immobilized as live and dead roots in the cropped plots. However, there was also considerable immobilization of fertilizer N in the manure and uncropped plots. This immobilization most likely occurred as microbial biomass and the roots of a few weeds and moss which were difficult to keep from the plots.

SECTION 3

RECOMMENDATIONS

These results demonstrate that the addition of manure with the fertilizer greatly increased denitrification of the fertilizer NO_3^-. Thus, it is recommended that manure not be applied with fertilizer. Manure applications should be timed such that the NO_3^- from fertilizer does not occur at the same position within the profile as does the carbon from manure. It also becomes important that water management be controlled even more carefully when manure is applied than with inorganic fertilizers in order to prevent anoxic development and denitrification. There is most likely some loss of N which is mineralized from the manure added to soil due to anoxic development during periods of high water content. Thus, the N in manure may not be as effective as an equal amount of N from inorganic fertilizers due to the inclusion of considerable carbon in the manure to increase denitrification.

Irrigation management practices directed at minimizing N loss from denitrification should be designed with the idea of maintaining soil-water pressure or water content within a range that anoxic conditions will most likely not develop for that part of the profile with the largest amount of carbon. For loam soil similar to Yolo, very little denitrification should occur if soil-water pressures are maintained smaller than -100 cm (-10 centibars) or tensions greater than 10 centibars. This limit of tension would be larger for a clay soil and smaller for a sandy soil. The degree of soil aggregation would also influence these limits.

Another management recommendation which may be made is that if water contents or pressures cannot be maintained outside the range where denitrification will occur, it may be possible to time fertilizer application so that NO_3^- will not occur in the zone along with the carbon at a time when water contents will be close to saturation. It may be possible, for instance, to apply NH_4^+ fertilizer immediately before a large irrigation for wetting a profile at the beginning of the irrigation season. The next irrigation would be timed and managed such that the NO_3^- would be moved out of the zone where most of the carbon occurs, yet remain within the zone where roots could obtain the N. This management approach would minimize the potential for denitrification in soils similar to the profile described in this report.

Field research should be conducted to determine such factors as the rate that microbial populations increase after irrigating an initially dry soil. Along with the population increase, the irrigation frequency and water contents maintained between irrigations should have an enormous influence on denitrification during normal irrigation cycles. Management decisions to maximize fertilizer use efficiency and minimize NO_3^- leaching to ground water

can be made only after the dynamics of microbial population growth, NO_3^- leaching, and denitrification rates in field sites are ascertained.

SECTION 4

EXPERIMENTAL PROCEDURES

FIELD INSTALLATION

Twelve, 1-m^2 field plots were established on Yolo loam soil (Typic Xerorthents) at Davis, California. The Yolo loam soil is a deep, well-drained, alluvial soil in the Sacramento Valley. The soil is a prominent agricultural soil of the area and is similar to other soils of extensive acreage. A schematic diagram of the experimental location and the treatment layout is given in Figure 1. Each of the 1-m^2 plots was established with a

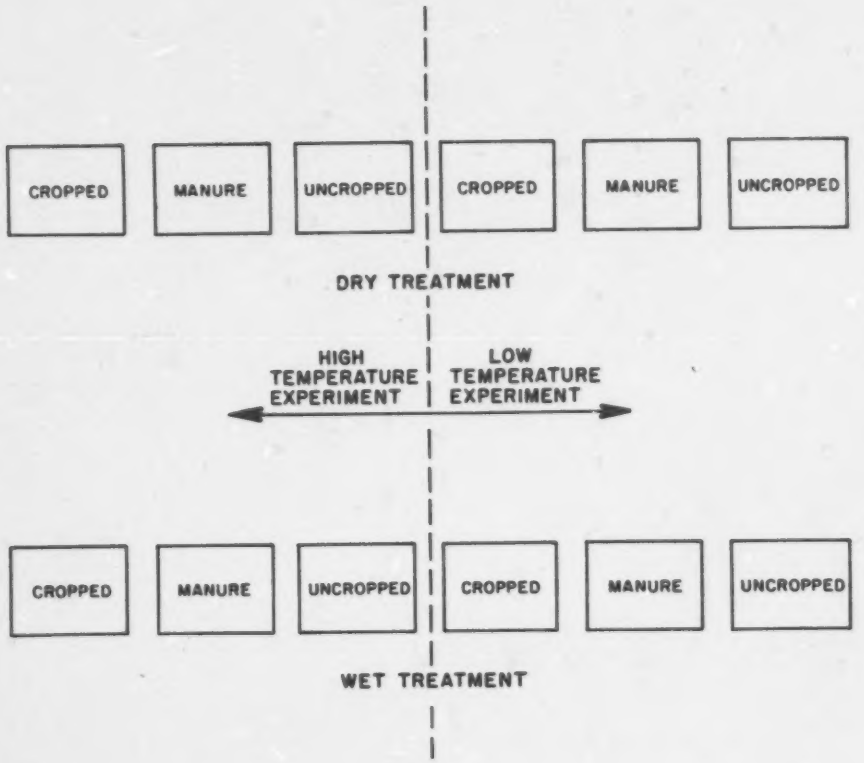

Figure 1. Schematic of plot layout and treatments.

60-cm deep redwood barrier around the outside edges of each undisturbed block of soil. The redwood barriers were installed by digging a trench around the 1-m^2 area, slipping the redwood over the undisturbed block of soil, and backfilling the trench on the outside of the redwood. The space between the redwood barrier and the soil on the inside was sealed by pouring melted paraffin into the small crack between the soil and the wood. Each of the twelve plots was instrumented with tensiometers, soil solution samplers, soil atmosphere samplers, and thermocouples. Five soil atmosphere samplers were installed at the 2-, 5-, 10-, and 15-cm depths; three soil atmosphere samplers were installed at the 20-, 30-, 60-, 90-, and 120-cm soil depths. Triplicate samplers, designed to function as tensiometers or solution extractors, were installed at the 60-, 90-, 120-, 150-, and 180-cm depths of the soil profile. Triplicate tensiometers were also installed at the 5- and 15-cm depths. Duplicate thermocouples were installed at the 5-cm depth. Soil solution samplers consisted of porous cups glued to polyvinyl chloride tubing. All of the deeper solution samplers and gas samplers were installed on an angle beginning on the outside of the 1-m^2 plot with the cup or the tip or the gas sampler ending up in the center of the 1-m^2 area of the plot. Soil atmosphere samplers consisted of 0.1 cm inside diameter nylon tubing glued into a 5-cm long perforated acrylic plastic tube. For the deeper soil depths the small diameter nylon tubing was placed inside a 1.3-cm diameter polyvinyl chloride tube and the nylon tubing glued into a milled plastic tip. For all samplers, the volume of the sampling tubes was very small. Soil solution samples were obtained by evacuating bottles connected to samplers. Soil atmosphere samples were obtained by withdrawing 1-ml increments of gas with plastic, disposable syringes. All gas samples were analyzed within a few hours after sampling.

Six plots were constantly maintained at a soil-water pressure head (h) very close to water saturation and six plots were maintained drier than near saturation but wetter than field capacity. The soil was maintained at a constant water content or pressure with a spray irrigation system which consisted of spray nozzles on a traveling boom. The system was activated by a timer so that plots could be irrigated on as frequent an interval as necessary to maintain constant soil-water content conditions.

In order to establish different carbon treatments within each of the two water regimes, two plots were cropped with perennial ryegrass (Lolium Perenne) for approximately 4 months prior to the experiment. Two plots remained uncropped, and manure at a rate of 3.4×10^4 kg ha^{-1} was mixed in the top 10cm of soil of four plots approximately two weeks before fertilizer was applied.

The two water content treatments and the three carbon treatments were also conducted at two times of the year in order to evaluate the effect of soil temperature on denitrification. One experiment was conducted in July when the average soil temperature at the 5-cm depth was approximately 23°C during the experimental period. Another experiment was conducted in January when the average soil temperature at the 5-cm depth was approximately 8°C during the experimental period. The entire experimental area was covered with plastic sheeting in order to prevent rain from changing the constant soil-water content conditions while experiments were being conducted.

The particle size analysis as a function of soil depth for the Yolo loam soil is given in Table 1 and the average bulk density at the field site is given as a function of depth in Figure 2. The bulk density is greatest near

TABLE 1. TEXTURE WITH SOIL DEPTH

Depth	Sand (%)	Silt (%)	Clay (%)	
0 - 15	41	37	22	Loam
15 - 30	40	37	23	Loam
30 - 60	42	38	20	Loam
60 - 90	38	42	20	Loam
90 - 120	38	42	22	Loam
120 - 150	32	46	24	Silt Loam
150 - 180	25	51		Silt Loam

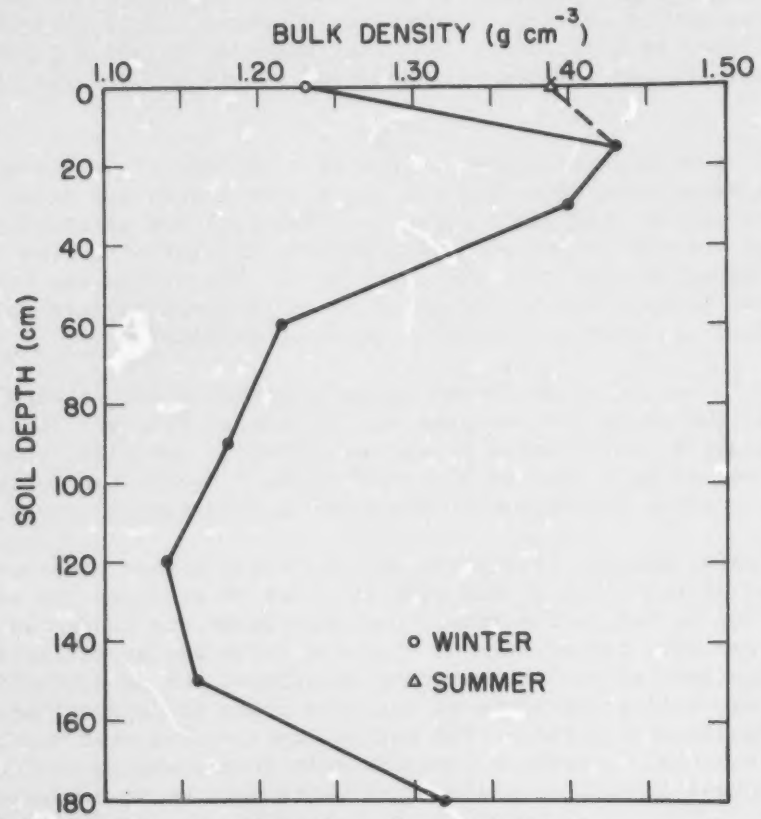

Figure 2. Bulk density as a function of soil depth for experimental area.

the soil surface with a minimum at the 120-cm depth. Bulk density was determined on 7.6 cm long, 7.6 cm diameter undisturbed soil cores.

The percentage of organic carbon as a function of soil depth for the uncropped and manure plots of the summer and winter experiments is given by Figure 3. Organic carbon was determined on soil samples taken after experi-

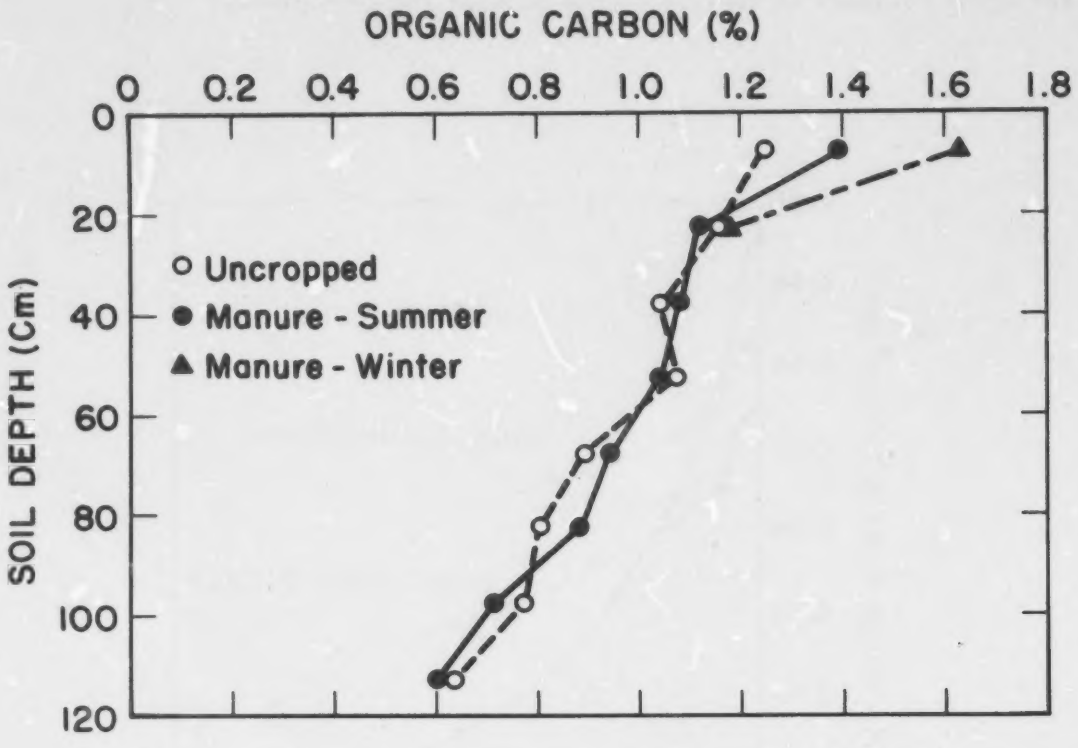

Figure 3. Organic carbon as a function of soil depth for the uncropped and manure plots of the summer and winter experiments.

ments were conducted, so several months had elapsed after manure application. The soil for organic carbon determination was ground to pass a 2mm sieve or finer. A subsample was then thoroughly ground with a pica mill to pass a 60 mesh sieve. Approximately 0.2 grams of the soil sample were placed in a crucible to which a small amount of iron and tin accelerator was added. The sample was covered with a single hole lid and placed into an induction furnace. The CO_2 produced was collected in a Nesbit tower containing ascarite. The tower was weighed before and after the burn to determine the amount of carbon dioxide trapped. There was no difference in the % carbon between a soil

sample that had been extracted with KCl and a sample that had not been extracted.

Figures 4 and 5 gives soil-water characteristic curves (soil-water content versus soil-water pressure) at several depths of the experimental site. The data points are the means of at least three 7.6-cm diameter, 7.6-cm long undisturbed soil cores. Figure 4 gives curves from surface cores obtained within the 1-m^2 plots of the wet (South) and dry (North) water treatments after the denitrification experiments were completed. Figure 5 gives curves for cores obtained at various depths outside the 1-m^2 plots.

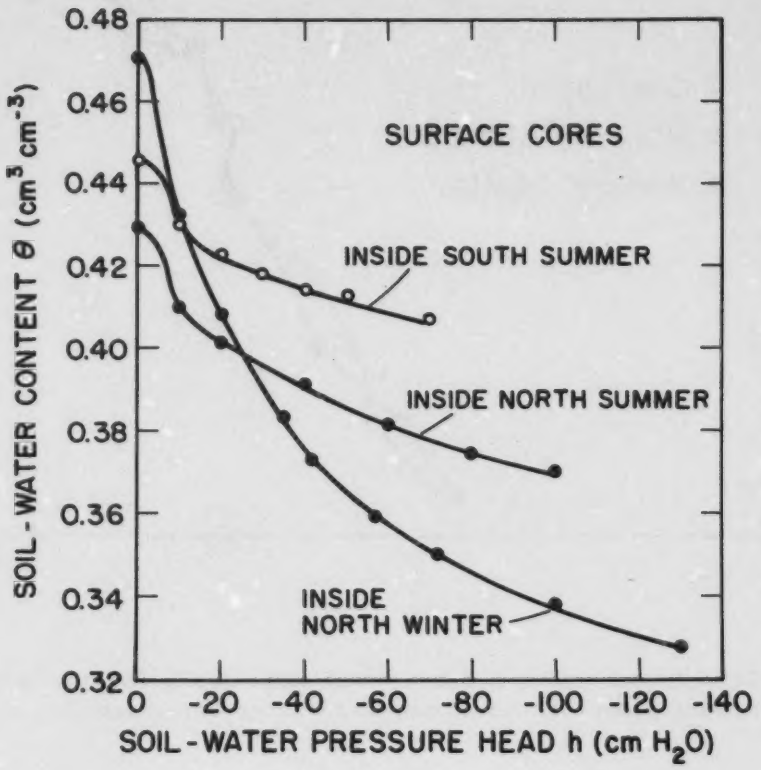

Figure 4. Soil-water content as a function of the soil-water pressure head for surface soil within plots.

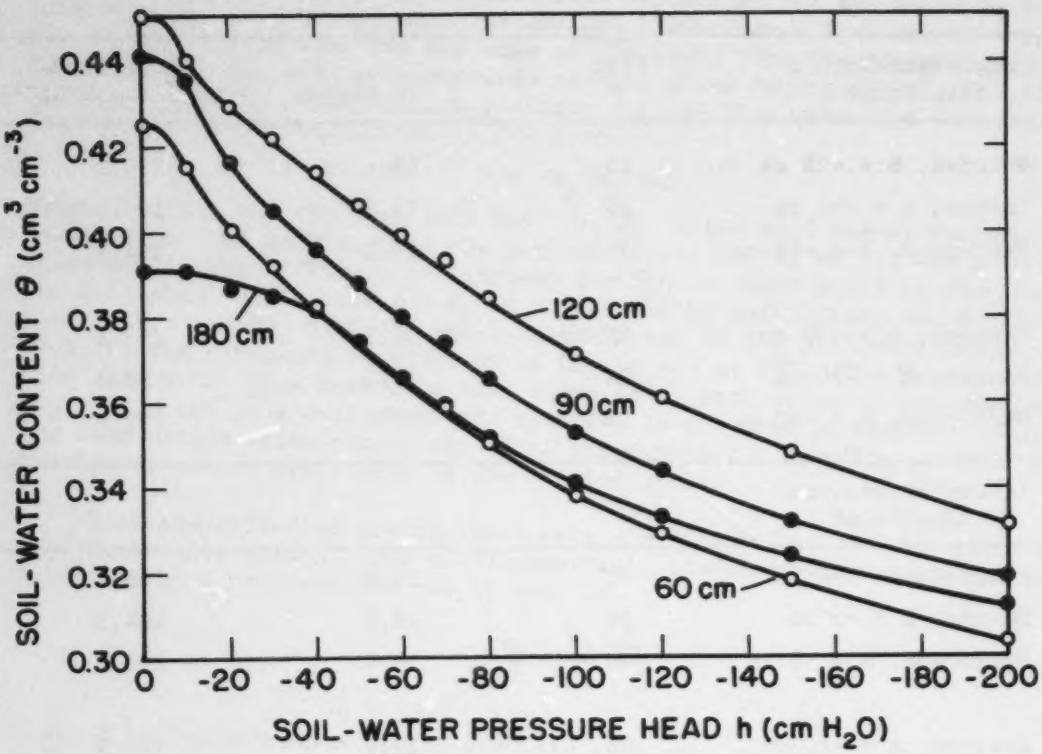

Figure 5. Soil-water content as a function of soil-water pressure head for several soil depths.

EXPERIMENTAL PROCEDURES - FIELD

After constant, steady-state water content conditions were achieved in the plots, NO_3^- solution equivalent to 300 kg N ha^{-1} was uniformly applied to the plots by applying approximately 3 ml of solution to each of 400 points at the soil surface. The ^{15}N enrichment of the added fertilizer was 20 and 40% excess ^{15}N for the wet and dry treatments, respectively. The actual amounts and enrichments applied to each plot are given in Table 2.

Within 6 hours after applying the fertilizer solution, an airtight cover was placed over the plots. The cover consisted of a thick sheet of acrylic plastic with rubber tubing on the lower edge to make an airtight seal with the top of the redwood border. Samples of the atmosphere beneath the cover were taken after one or two hours with the lid in place and analyzed for $^{15}N_2$ and $^{15}N_2O$. Soil atmosphere samples from within the soil profile were also taken soon after applying the fertilizer. Soil atmosphere samples were taken

TABLE 2. FERTILIZER APPLICATION AND ^{15}N ENRICHMENT OF EACH TREATMENT

High-Temperature Experiment	Plot #	% ^{15}N Excess	Fertilizer Rate (kg N ha^{-1})
Cropped, h = -15 cm	1S	19.4	296.0
Manure, h = -15 cm	2S	19.3	300.6
Uncropped, h = -15 cm	3S	19.2	304.9
Cropped, h = -70 cm	1N	38.3	297.4
Manure, h = -70 cm	2N	39.2	298.4
Uncropped, h = -70 cm	3N	38.4	292.8
Low-Temperature Experiment			
Cropped, h = -8 cm	4S	19.8	299.9
Manure, h = -8 cm	5S	19.8	294.3
Uncropped, h = -8 cm	6S	19.4	294.0
Cropped, h = -50 cm	4N	39.9	296.5
Manure, h = -50 cm	5N	40.0	297.6
Uncropped, h = -50 cm	6N	39.6	294.2

in 1-ml aliquots and N_2O, CO_2, O_2, and N_2 analyzed by gas chromotography in the laboratory. Another 0.5 to 1 ml of gas was taken to determine $^{15}N_2$ with a mass spectrometer. All soil samples to be analyzed by mass spectrometry were pulled through ascarite, dehydrite (magnesium perchlorate), and a commercial O_2 scrubber. Gas samples from the profile and samples from beneath the cover were taken daily for a few days after the fertilizer was applied and then at less frequent intervals until $^{15}N_2$ and $^{15}N_2O$ could no longer be detected above background.

Soil solution samples were taken at weekly intervals. The grass of the cropped plots was cut periodically, and the total clippings dried for analysis. After the NO_3^- had been completely leached through the 180-cm depth of the wet treatments, both the wet and dry plots were allowed to dry and soil samples taken in 15-cm increments down to 120 cm. The samples consisted of eight separate holes taken with a Veihmeyer tube within the 1-m^2 plot. On some plots, each of these samples was run individually. On others, the eight

samples from each depth were combined into two samples at each depth.

Soil gas-diffusion coefficients were determined for the plots by the CO_2 flux method. This method measures the CO_2 trapped in a NaOH solution from an air stream flowing over the top edge of the plot. The CO_2 concentration gradients within the soil were measured several times during the CO_2-trapping process. The CO_2 concentration gradient and CO_2 flux were used in calculating the diffusion coefficient of CO_2 from

$$f = -D_p(\partial C/\partial x) \qquad (1)$$

where f is the gas flux (mg cm^{-2} day^{-1}), D_p is the soil gas-diffusion coefficient (cm^2 day^{-1}), C is the gas concentration (mg cm^{-3}), and x is distance (cm). The diffusion coefficient for N_2O is about equal to that for CO_2. The diffusion coefficient for N_2 is calculated by multiplying the diffusion coefficient for CO_2 by 1.25, which is the ratio of the diffusion coefficient of N_2 to the diffusion coefficient of CO_2 in air at 0°C. The basic assumption in the CO_2 flux method is that there is no production or consumption of CO_2 within the zone over which the gradient is measured or beneath the cover and that steady-state conditions exist throughout the sampling period. Thus, the method is not applicable to the cropped plots.

Soil gas-diffusion coefficients were also determined for the plots by a transient-state method. The one-dimensional, transient-state equation for diffusion of a non-reactive gas in soil is

$$\frac{\partial C}{\partial t} = \frac{D_p}{\varepsilon}\frac{\partial^2 C}{\partial x^2} \qquad (2)$$

where C is concentration of the gas with reference to the gas phase (cm^3 gas cm^{-3} soil air), t is time (hours), D_p is the soil gaseous diffusion coefficient (cm^2 $hour^{-1}$), ε is the soil-air content (cm^3 air cm^{-3} soil), and x is soil depth (cm). Values of D_p and ε are assumed to be constant with respect to x and t. Equation (2) was solved analytically using a time-dependent upper boundary condition. Such a condition could be easily achieved experimentally by feeding gas at a constant rate into an enclosed chamber above the soil with ports for the mixed gas to leave the chamber. If N_2 is the gas of interest, the N_2 concentration within a chamber above the soil could be decreased with time by feeding gas of zero N_2 concentration into the chamber with the mixed gas leaving the chamber through exit ports. The N_2 concentration at the soil surface would decrease as some function of time. For the general case where the concentration at the soil surface varies with time by a smooth function, the surface condition may be described by a step function given by

$$
\begin{aligned}
C(0,t) = S_o \qquad & t_o < t \leq t_1 \\
S_1 \qquad & t_1 < t \leq t_2 \\
S_2 \qquad & t_2 < t \leq t_3 \\
\cdot \qquad & \cdot \\
\cdot \qquad & \cdot \\
S_k \qquad & t_k < t \leq t_{k+1} \\
\cdot \qquad & \cdot \\
\cdot \qquad & \cdot \\
S_n \qquad & t_n < t
\end{aligned} \tag{3}
$$

where S_k is the surface concentration within any time interval k. The solution of Eq. (2) using Eq. (3) and

$$C = S_o \qquad x \geq 0 \qquad t = 0 \tag{4a}$$

$$C = S_o \qquad x \to \infty \qquad t \geq 0 \tag{4b}$$

is

$$C(x,t) = S_o + \sum_{k=1}^{L} (S_k - S_{k-1}) \operatorname{erfc} \{x/[2\sqrt{D_m(t-t_k)}]\} \tag{5}$$

where $L = \{k: t > t_k\}$, that is, k is the largest integer such that t_k is less than t, $D_m = D_p/\varepsilon$, and k is a dummy variable. The only assumptions inherent in the use of Eq. (5) for determining the diffusion coefficient are that D_m is constant with respect to x and t and that diffusion is not allowed to proceed so long that concentrations markedly change at the bottom of a field box.

The general procedure for determining the diffusion coefficient D_m was to fit Eq. (5) to concentration profiles measured in the field at several times, using values of S_k and t obtained from interpolation of measured values at the surface and at t = 0, and various values of D_m. The least absolute difference was used to evaluate the best fit of the predicted to the measured profiles. The use of the absolute difference gave a more clearly defined minimum (best fit) than did least squares.

ANALYTICAL TECHNIQUES

Oxygen, N_2, CO_2, and N_2O were analyzed by gas chromotography with a thermal conductivity detector. The concentration of N_2O in the gas samples was determined by chromatography with a helium ionization detector according to the procedure described by Delwiche and Rolston (1976).

The isotopic composition of N in gas samples was determined on samples scrubbed for O_2, CO_2, and H_2O by direct injection into the mass spectrometer. An independent experiment was conducted in which manure was added to soil in order to determine if gaseous compounds were being evolved from the manure and soil mixture which would interfere with the $^{15}N_2$ analyses. These experiments showed that no such evolution occurred to any significant degree.

Soil samples were analyzed for extractable and digestible nitrogen and soil solution samples were analyzed for NH_4^+, NO_2^-, and NO_3^-. The soil sample was extracted with 1.0 N KCl and the solution analyzed by MgO-Devarda alloy reduction technique. The extraction procedure removed solution NH_4^+, NO_2^-, NO_3^-, and exchangeable NH_4^+. The NH_4^+ and NO_2^- concentrations in all soil and soil solution samples were negligible. The Kjeldahl method was used to determine the total digestible N in the soil and plant samples. Two-g samples of soil were digested with 36N H_2SO_4 and salts (K_2SO_4, $CuSO_4$, and selenium) for approximately 17 hours to convert the N to NH_4^+. The same procedure was used for the plant digests except that 0.25 g of plant material was used, and digestion time was 6 hours. The N in the digests was determined by titration of the NH_4^+ liberated by distillation of the digest with 40% NaOH. Detailed procedures for determination of N in soil, plant, and soil solution samples are given by Bremner (1965).

SECTION 5

RESULTS AND DISCUSSION

HIGH-TEMPERATURE EXPERIMENT

Plot Characteristics

Temperature at the 5-cm soil depth as a function of time after the fertilizer was applied to the plots of the summer experiment is given by Figure 6.

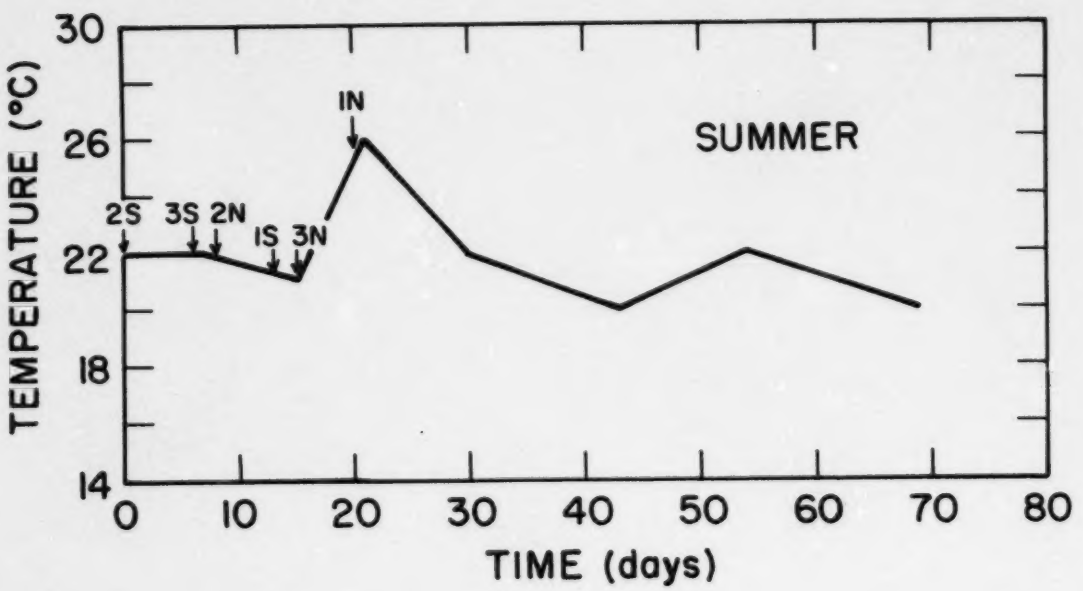

Figure 6. Mean soil temperature of two probes at the 5-cm soil depth of six plots as a function of time after fertilizer was applied to the plots of the summer experiment. The arrows give the fertilizer application for each plot with the symbols given in Table 2.

The arrows give the time that fertilizer was applied to particular plots. The average soil temperature during most of the denitrification activity was approximately 23°C. There was a slight increase in soil temperature beginning about two weeks after the fertilizer was applied to the first plot. The increase in soil temperature occurred at the time fertilizer was applied to the cropped and uncropped plots of the dry treatment.

The increase in soil temperature at two weeks after fertilizer was applied to the first plot coincided with a decrease in the soil-water pressure of the dry plots. The soil-water pressure head, h, for the 5- and 15-cm depths as a function of time after fertilizer application for the summer experiment is given by Figure 7. For the h = -15 cm and h = -70 cm soil-water

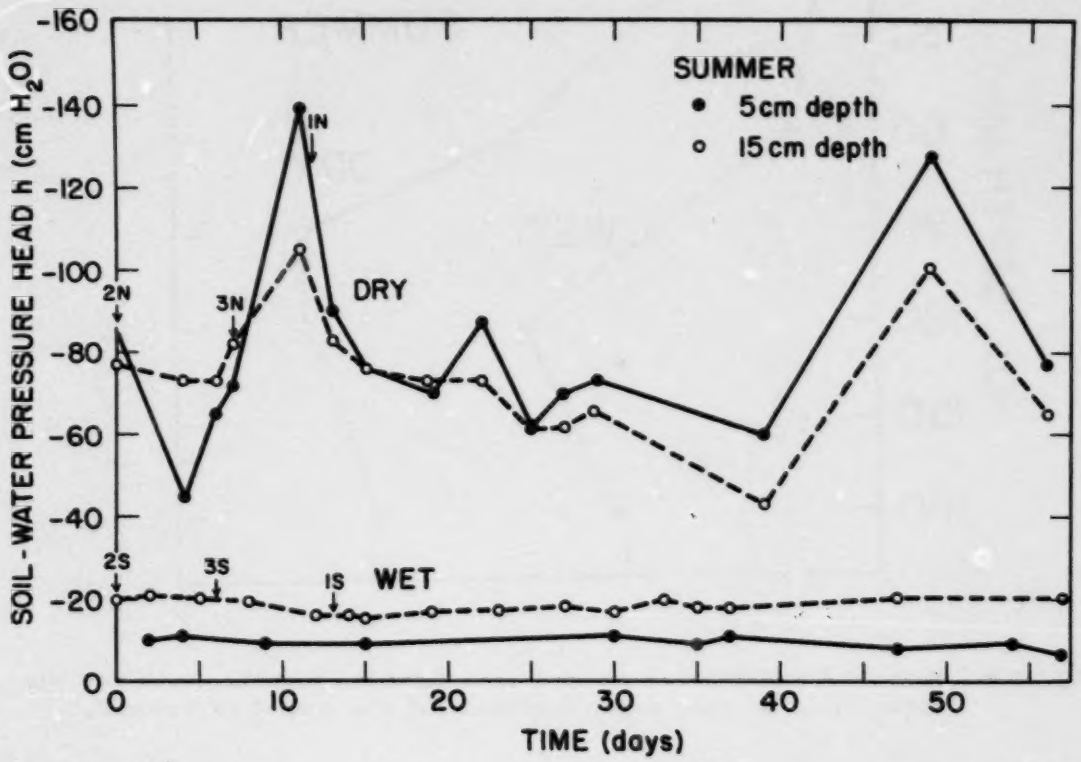

Figure 7. Mean soil-water pressure head of three tensiometers in each plot at the 5- and 15-cm soil depth as a function of time after fertilizer application to the two water treatments of the summer experiment. The arrows give the fertilizer application for each plot with the symbols given in Table 2.

pressure treatment, the soil-water pressure head for the h = -15 cm treatment was relatively constant throughout the denitrification period, whereas the

soil-water pressure for the h = -70 cm treatment varied due to changing temperature and radiation conditions. Soil-water pressure values were maintained by reading tensiometers daily and making changes in number of passes of the irrigation system in order to correct any increases or decreases in the soil-water pressure head from the desired values. It was sometimes difficult to maintain constant water content in the h = -70 cm plots during rapid changes in air temperature. Values of the soil-water pressure head as a function of depth are given by Figure 8 for the h = -15 and -70 cm treatments.

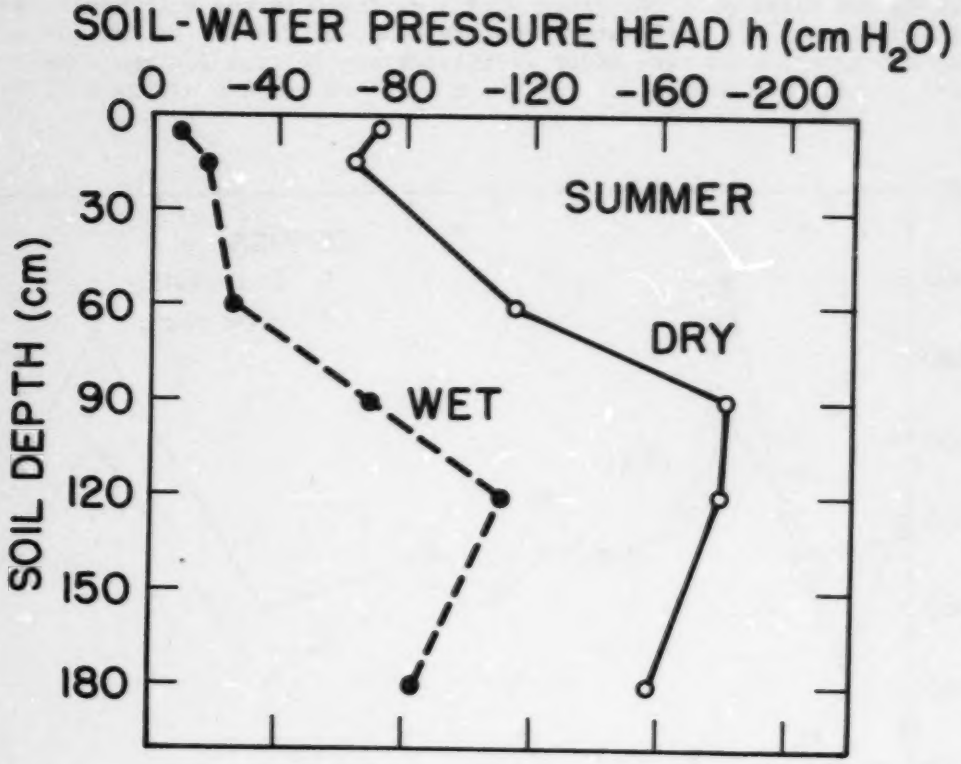

Figure 8. Mean soil-water pressure head as a function of soil depth for the three plots of each water treatment of the summer experiment.

The soil-water pressure head values are average numbers of the three plots of each soil-water treatment. In a similar manner the soil-water content, θ, as a function of depth for the two water treatments is given in Figure 9. It is obvious from Figures 8 and 9 that soil-water content and soil-water pressure both decrease with depth. This is due primarily to the fact that the soil surface tended to seal with time resulting in lower infiltration rates in the surface than in the remainder of the profile. This characteristic of decreasing water contents and pressures with depth results in the possibility of

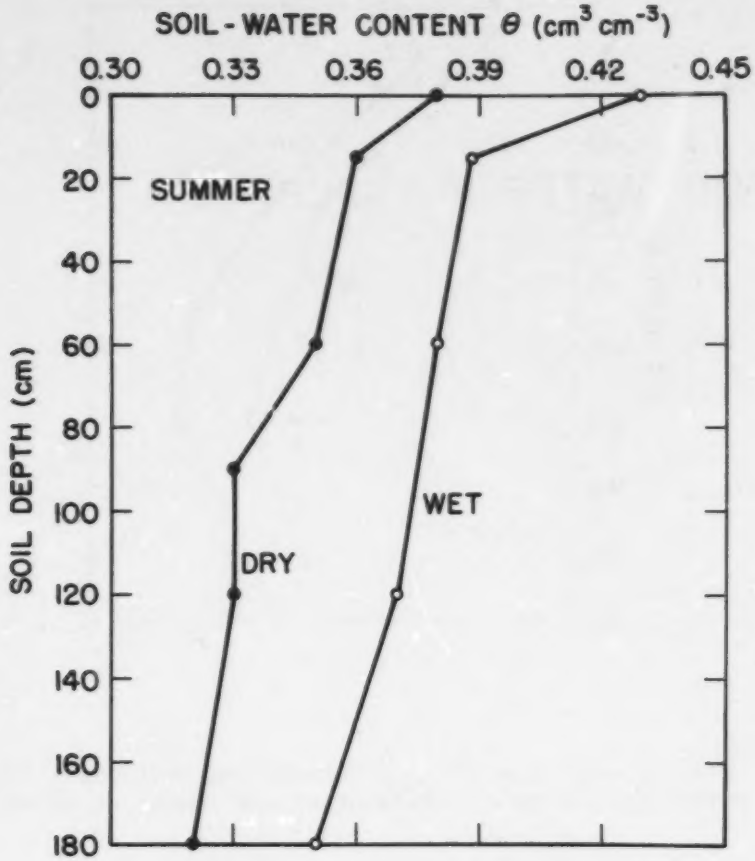

Figure 9. Mean soil-water content as a function of soil depth for the three plots of each water treatment of the summer experiment.

limited denitrification occurring in the lower part of the profile. From soil-water content and soil bulk density, the soil-air content, ε, as a function of depth can be calculated and is plotted in Figure 10 for the two soil-water treatments. These values of ε are average values for the three plots of each water treatment. The $h = -15$ cm and $h = -70$ cm treatments result in only very small differences between the soil-air content in the surface soil. However, as will be shown later, this small difference is sufficient to make a very large difference in the denitrification rate and magnitude.

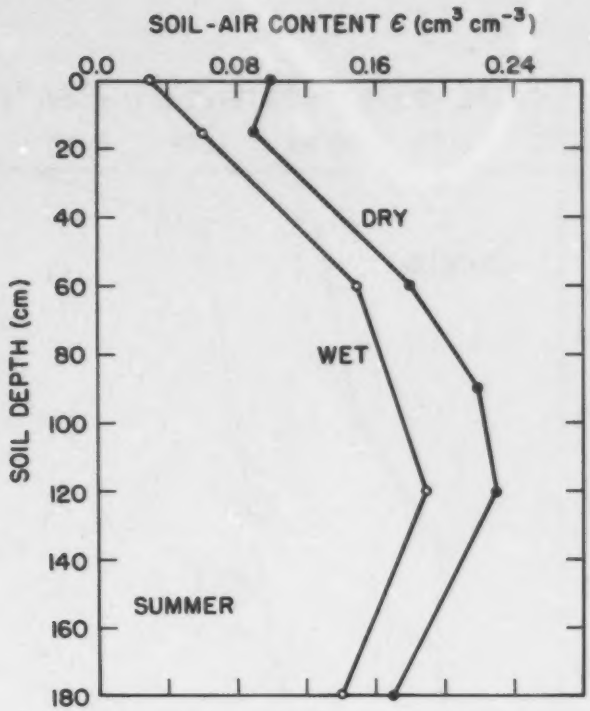

Figure 10. Mean soil-air content as a function of soil depth for the three plots of each water treatment of the summer experiment.

Soil Gases

The amount of O_2 in the soil and the diffusion rate of O_2 within the soil profile is one of the very important factors determining whether denitrification will occur or not. Figure 11 gives O_2 concentrations within five plots of the summer experiments as a function of soil depth. Although measurements were not made on the uncropped, h = -15 cm treatment, the O_2 concentration would be expected to be no smaller than 10%. The oxygen concentrations were measured during the time of the denitrification experiments.

For the three plots at h = -70 cm, O_2 values decreased to no less than approximately 16% and that occurred in the plot to which manure had been added. For the plots maintained at a soil-water pressure head of -15 cm, O_2 values became as small as 9% at the 20-cm depth of the cropped plot and as low as approximately 3% at the 10-cm depth in the plot to which manure had been added. In all cases, the smallest concentration of O_2 occurred at the 10-to 20-cm

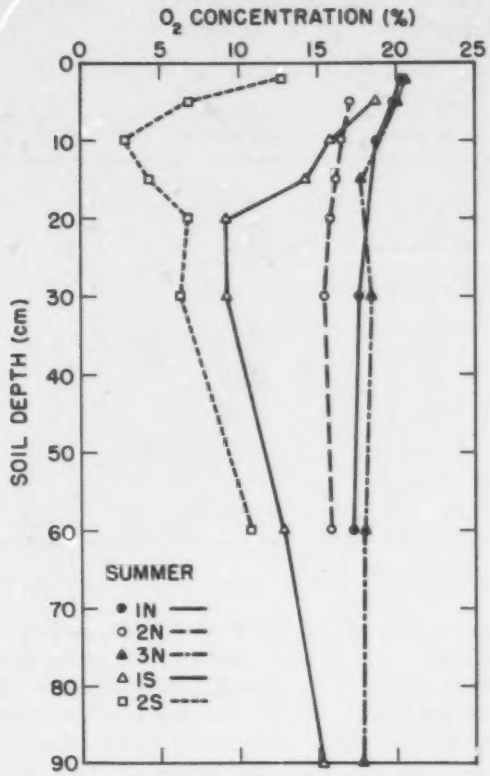

Figure 11. Oxygen concentration as a function of soil depth in the plots of the summer experiment. Symbols are given in Table 2.

depth in the profile with higher concentrations toward the soil surface and also higher concentrations deeper with depth in the profile. This phenomenon has also been observed by Rolston et al. (1976) where O_2 levels were smallest near the soil surface and increased with depth due to smaller soil-water pressures, smaller water contents, and more diffusion of O_2 from the deeper depths of the soil profile. Since these samples were determined by extracting a volume of gas with a syringe, the concentrations reported here are most likely those concentrations in the large, continuous pores of the soil profile. Thus, the O_2 concentrations only give a qualitative estimate of the anoxic conditions within the profiles.

Table 3 gives initial concentration of N_2O within the six plots of the summer experiment before application of NO_3^- fertilizer. This gives an idea of the degree of reducing conditions within the profiles and the denitrification of native nitrogen. These data indicate that the N_2O concentration before fertilizer application was dependent upon the reducing conditions of

TABLE 3. CONCENTRATION (PPMV) of N_2O WITHIN PROFILES BEFORE APPLICATION OF FERTILIZER OF THE SUMMER EXPERIMENT. AMBIENT CONCENTRATION OF N_2O IN AIR IS APPROXIMATELY 0.30 PPM

Soil Depth (cm)	h = -15 cm			h = -70 cm		
	Cropped	Manure	Uncropped	Cropped	Manure	Uncropped
2	0.08	4.0	2.6	0.81	32	1.33
5	0.09	2.6	3.1	0.46	39	0.71
10	0.09	6.8	3.3	0.23	40	1.19
15		32.4	3.3			
20	0.19	26.3	3.0	0.78	37	1.06
30	0.37	38.4	3.5	0.96	41	1.52
60	0.29			1.2	30	4.31
90	1.25	9.2			16	

the profile and the amount of soil nitrogen available. The concentrations in the cropped plots were initially near ambient. This was most likely due to the grass using nitrogen which was slowly mineralized from soil organic matter and to the reducing conditions within the root zone caused by root and microbial respiration with the overall result of reduction of any N_2O to N_2. Almost all samples from the h = -15 cm, cropped plot were below ambient indicating very little production of N_2O or reduction of N_2O to N_2. The manure plots initially had N_2O concentrations ranging from 2 to 41 ppm. Apparently there was some denitrification of nitrogen mineralized from the manure. The h = -70 cm manure treatment had generally higher N_2O concentrations than did that of the h = -15 cm, manure treatment. Nitrous oxide concentrations in the uncropped plots ranged from .7 to 4 ppm. Apparently there was some mineralization of soil organic matter in the uncropped plots resulting in a small amount of N which could be denitrified forming N_2O. However, conditions were apparently not anoxic enough that the N_2O was further reduced to N_2.

Representative N_2O concentration profiles from denitrification of the added fertilizer as a function of soil depth for two days after fertilizer application for the h = -15 cm treatments are given by Figure 12. The concentration profiles demonstrate the enormous differences in N_2O production among the cropped, manure, and uncropped plots. It appears that the greatest denitrification in the manure plot was occurring in the upper 10 cm of soil, whereas denitrification in the cropped plot appeared to be occurring slightly deeper. Similar data for the plots of the h = -70 cm treatment for two days after application of fertilizer are shown by Figure 13. There was much less production of N_2O in the h = -70 cm treatments than in the h = -15 cm treatments. Since N_2O concentrations did not become great enough to measure ^{15}N without concentrating the N_2O sample, N_2O concentrations greater than initial values were considered to be derived from the fertilizer.

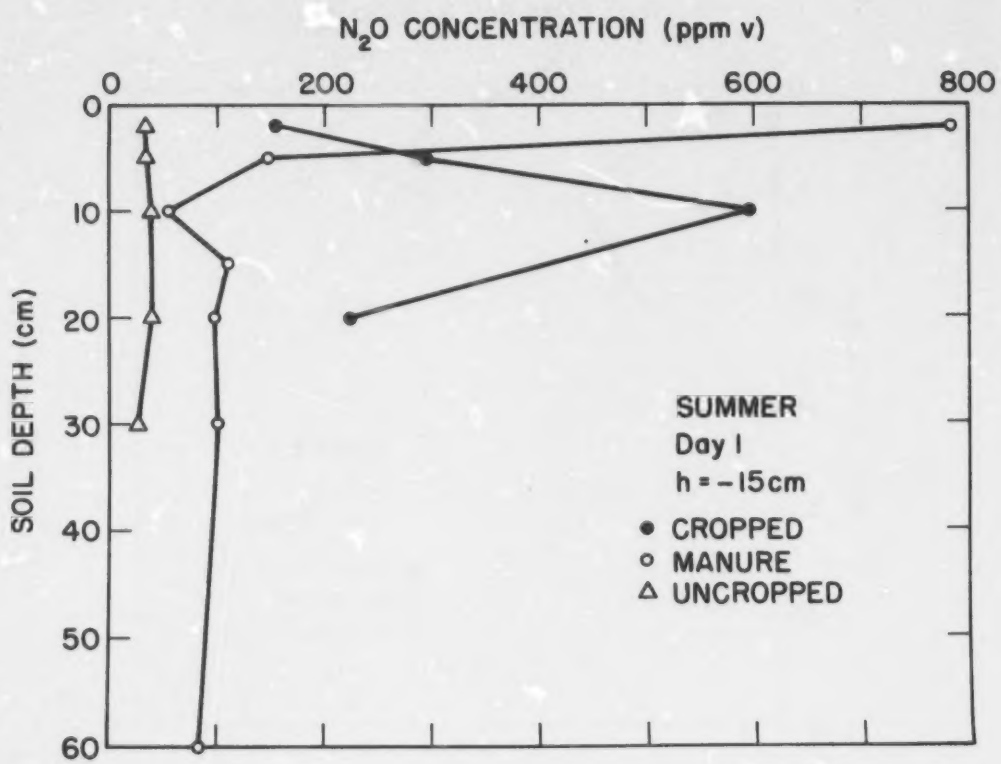

Figure 12. Nitrous oxide concentration with depth on one day in the h = -15 cm treatment of the summer experiment.

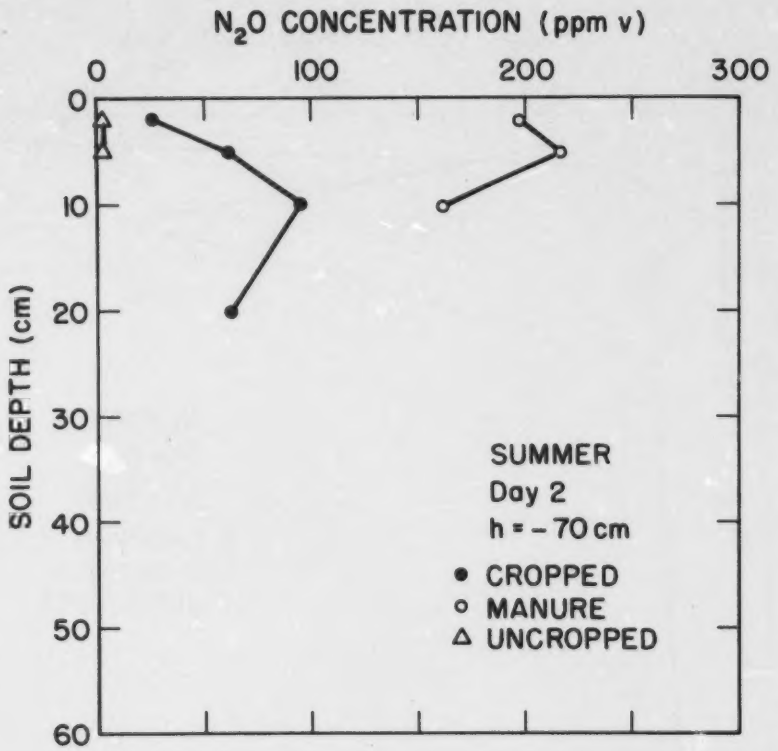

Figure 13. Nitrous oxide concentration with depth on one day in the h = -70 cm treatment of the summer experiment.

Similar representative N_2 profiles derived from the fertilizer for two days after application of the fertilizer are given in Figures 14 and 15 for the h = -15 and h = -70 cm treatments, respectively. The concentration profiles for $^{15}N_2$ gas follow the same pattern as do those of the N_2O, with considerable differences in $^{15}N_2$ production among the cropped, manure, and uncropped plots.

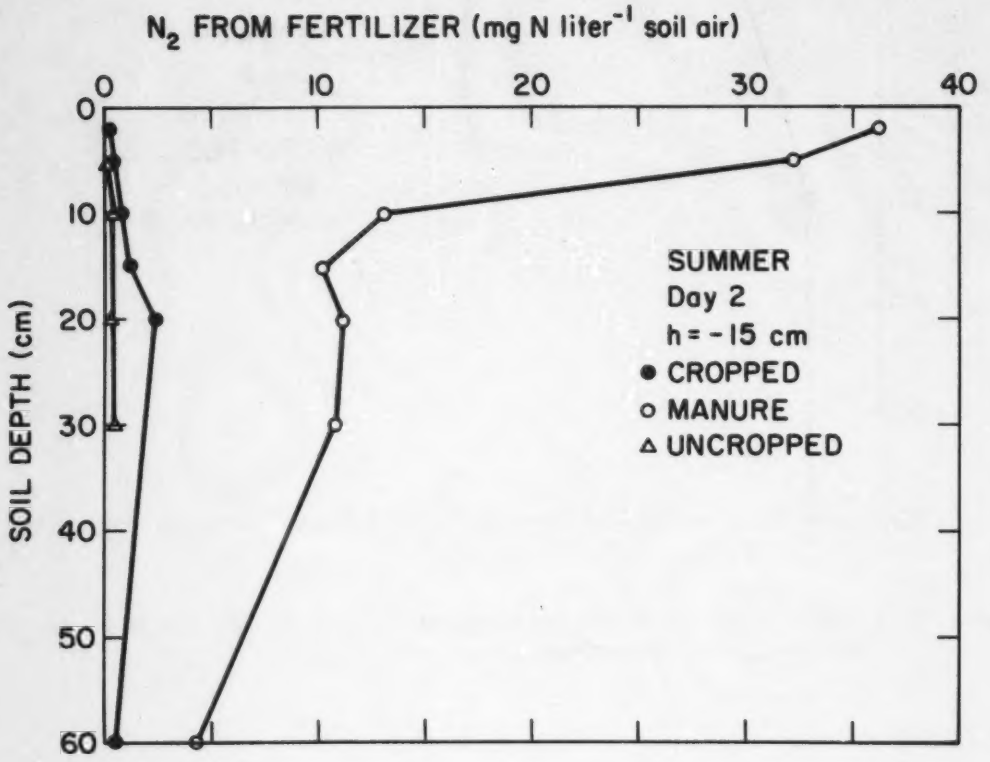

Figure 14. Concentration of $^{15}N_2$ with depth on one day in the h = -15 cm treatment of the summer experiment.

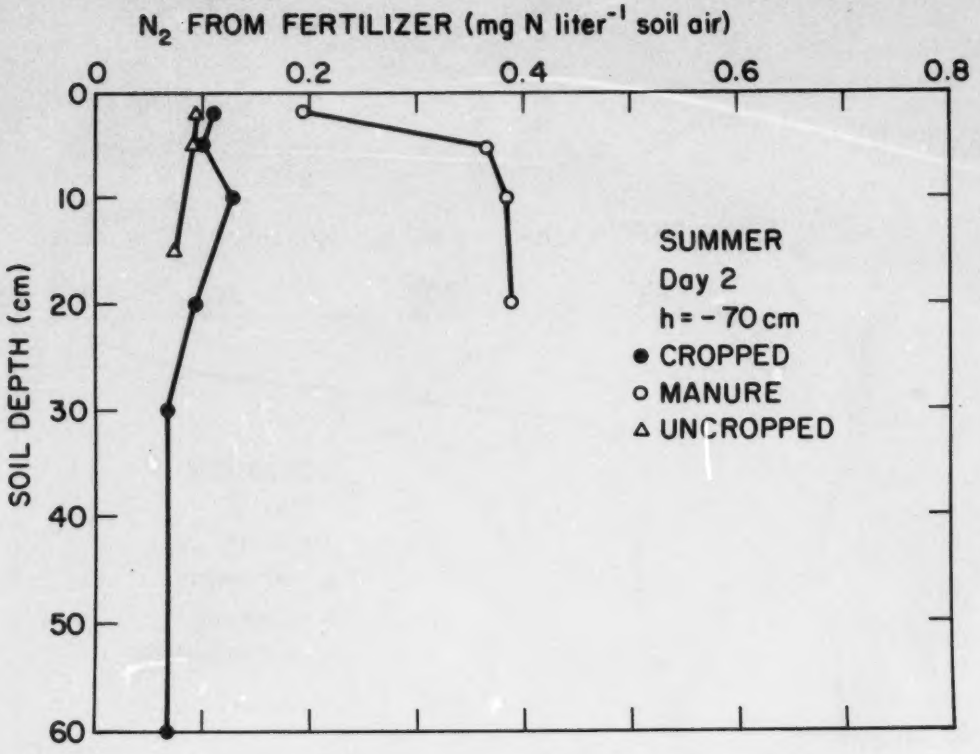

Figure 15. Concentration of $^{15}N_2$ with depth on one day in the h = -70 cm treatment of the summer experiment.

Gas Fluxes

Flux of N_2O derived from the fertilizer as a function of time for the manure and cropped plots is given by Figure 16. These fluxes were determined from the accumulation of N_2O beneath a cover placed over the soil surface for 1- or 2-hour intervals. The time interval that the covers remained on the plots was calculated from the air volume of the cover above the soil, the enrichment of the fertilizer, the minimum detectable limit of $^{15}N_2$ by the mass spectrometer, and the criterion that an N_2 flux of at least 1.0 kg N ha^{-1}day^{-1} was measurable. The numbers below each of the soil-water pressure head treatments are total N_2O produced as determined from the area beneath each of the flux versus time curves. The flux calculated from the concentration increase beneath the cover was corrected for the decrease in the concentration gradient with time as the gases accumulated. The decrease in the concentration gradient with time would result in an underestimation of the diffusive flux as measured from concentration changes beneath the cover. A simple correction for this underestimation of the flux can be made based upon the steady-state

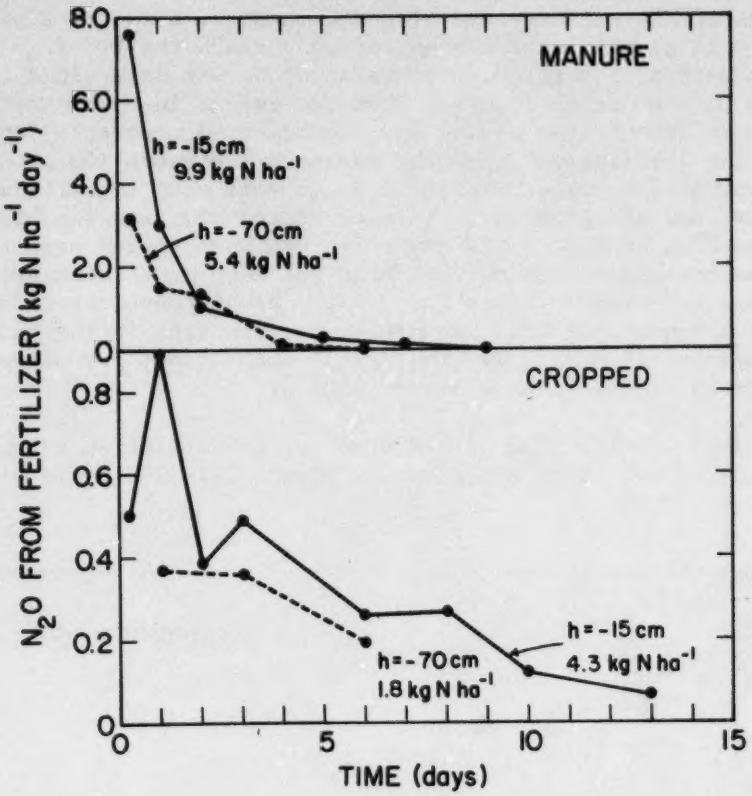

Figure 16. Flux of N_2O calculated from measurements beneath cover with time for the manure and cropped plots of the summer experiment.

diffusion equation,

$$f = -D_p(dC/dx) \tag{6}$$

where f is the gaseous flux, D_p is the soil gaseous diffusion coefficient, C is gas concentration, and x is soil depth. If it is assumed that the concentration at the soil surface is equal to the concentration beneath the cover and that the concentration at the shallowest sampling depth (2 cm) does not change with time, the following boundary conditions apply:

$$C = C_o \quad , \quad x = 0 \text{ cm} \tag{7a}$$

$$C = C_2 \quad , \quad x = 2 \text{ cm} \tag{7b}$$

The solution to Equations (6) and (7) rearranged to solve for D_p is

$$D_p = -(VL)(At)^{-1}\ell n[(C_2-C_o)/C_2] \tag{8}$$

where V is the volume of the chamber placed over the soil surface, L is the depth of soil for which measurements are taken (2 cm), A is the cross-sectional area of the soil covered with the chamber, t is the time after covering the soil at which the concentration beneath the lid (C_o) was measured, and ℓn is the natural logarithm. The value of D_p was determined from Equation (8) for the 0 to 2-cm depth interval from the change in concentration (C_o) of N_2O over a 1- or 2-hour time period and the measured concentration at the 2-cm depth (C_2). The calculated D_p and the measured concentration gradient (dC/dx) at t = 0 (assumed to be linear for 0 to 2 cm) were used to calculate the corrected flux from Equation (6). This corrected flux was the best estimate of the gaseous flux of N_2O if the cover had not been placed over the soil surface. Measurements of concentration at the 2-cm depth both before and after the cover had been in place for 2 hours demonstrated that Condition (7) was valid for a 2-hour period. The greatest correction in the calculated flux was for the cropped (h = -15 cm) treatment. Corrections for all other plots were less than 5% of the total denitrification.

Similar data for the flux of N_2O from the fertilizer as a function of time for the uncropped plots are given by Figure 17. The scale of the

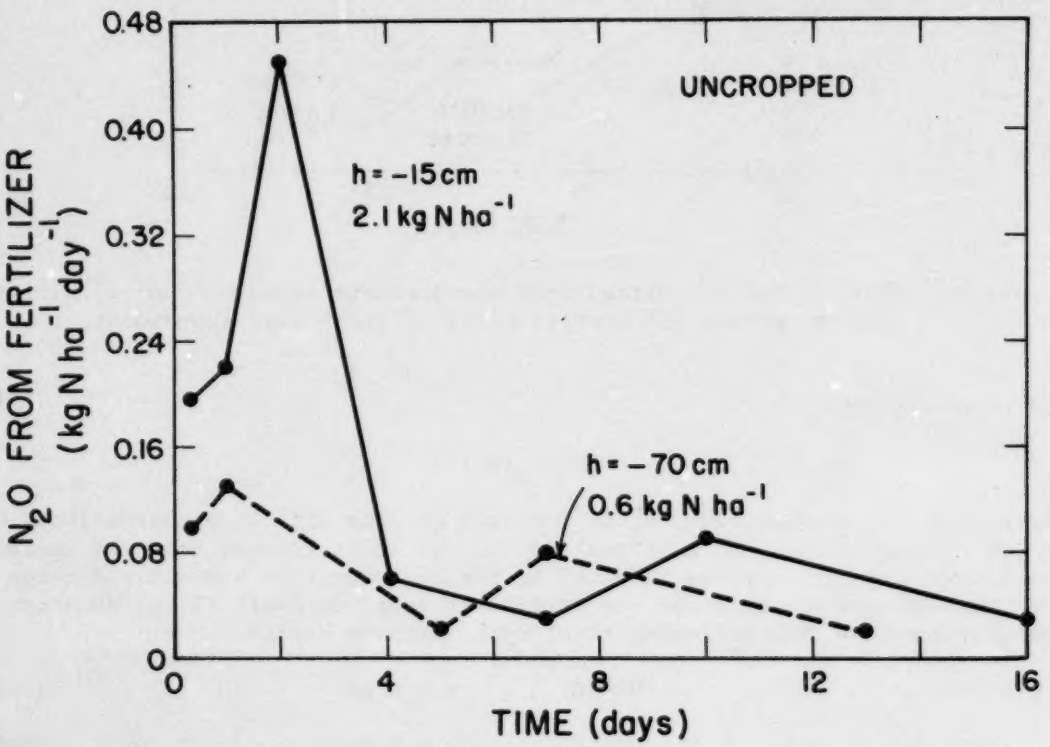

Figure 17. Flux of N_2O calculated from measurements beneath cover with time for the uncropped plots of the summer experiment.

ordinate is considerably smaller than that for the cropped and manure plots. Both Figures 16 and 17 show that N_2O could not be detected beneath the lid after approximately 20 days.

Similar data for the flux of N_2 derived from the fertilizer as a function of time for the manure and cropped plots are given by Figure 18. These fluxes

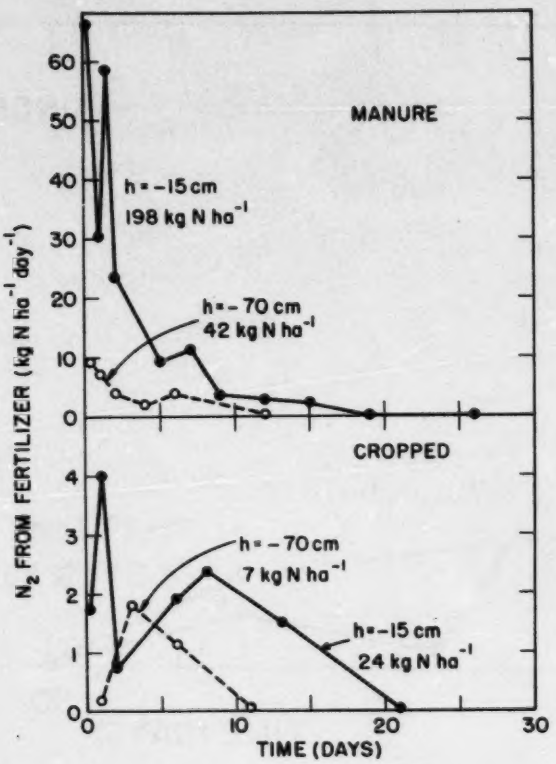

Figure 18. Flux of $^{15}N_2$ calculated from measurements beneath cover with time for the manure and cropped plots of the summer experiment.

were also determined from the accumulation of N_2 beneath a cover placed over the soil surface and corrected for the decrease in the concentration gradient as N_2 accumulated. The numbers below each of the soil-water pressure head treatments are total N_2 produced.

The increase in the N_2 flux at 1.4 days of the h = -15 cm, manure treatment (Figure 18) was from a sample taken in the afternoon of a fairly hot day. Thus, the fluxes may be slightly underestimated for a few days after application due to increased denitrification as surface soil temperature increased in the afternoon. The increase in the N_2 flux for the h = -15 cm, cropped

treatment at approximately 3 days after the fertilizer was applied coincided with the increase in temperature (Figure 6). The N_2 flux from the uncropped, h = -70 cm treatment would also be expected to increase due to the temperature increase. There appeared to be a slight increase in flux although the total flux was small and any increase would have a small effect. Data for the flux of N_2 from the fertilizer as a function of time for the uncropped plots are given by Figure 19. The scale of Figure 19 is considerably different than

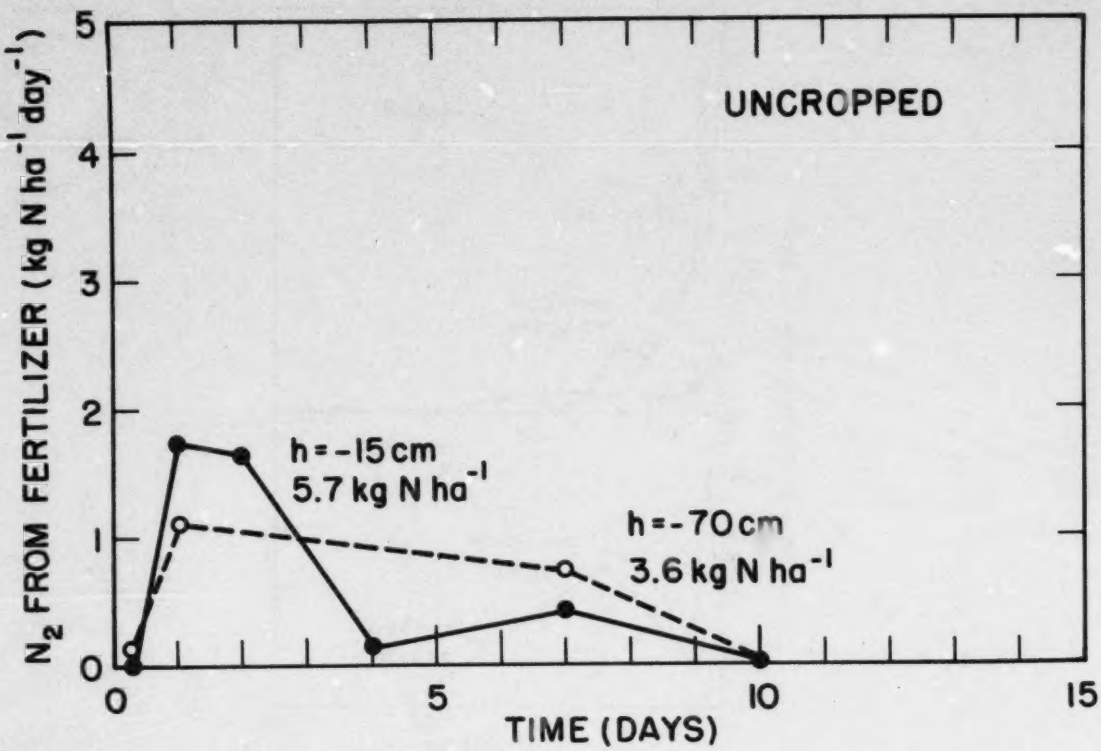

Figure 19. Flux of $^{15}N_2$ calculated from measurements beneath cover with time for the uncropped plots of the summer experiment.

that of Figure 18. The very high initial N_2 denitrification rate and rapid decrease in the rate are similar to the behavior of the N_2O flux. In all cases, the amount of N_2 produced was much greater than N_2O.

The data given in Table 4 are the total amount of denitrification consisting of both N_2 and N_2O for the six treatments of the summer experiment as determined from measurements beneath a cover placed on the soil surface over the time period for which N_2 and N_2O were measureable. The amount of denitrification ranged from 1% for uncropped, h = -70 cm treatment to 69% for the

TABLE 4. DENITRIFICATION AS N_2O, N_2, AND TOTAL FOR THE SUMMER EXPERIMENT AS DETERMINED FROM MEASUREMENTS BENEATH A COVER PLACED OVER THE SOIL

Treatment	N_2O (kg N ha^{-1})	N_2 (kg N ha^{-1})	Total (kg N ha^{-1})	Total (% of fertilizer)
Manure, h = -15 cm	9.9	198	208	69
Manure, h = -70 cm	5.4	42	47	16
Cropped, h = -15 cm	4.3	30	34	11
Cropped, h = -70 cm	1.8	7	9	3
Uncropped, h = -15 cm	2.1	5.7	8	3
Uncropped, h = -70 cm	0.6	3.6	4	1

manure, h = -15 cm treatment. It is obvious that water content and carbon level had an enormous influence on the total denitrification.

The N_2 to N_2O ratio as a function of time after application of the NO_3^- to each of the plots is given in Table 5. The average ratio calculated on the basis of total amount of each gas produced is also given. The largest ratio of 20.0 occurred for the manure treatment at the soil-water pressure head of -15 cm. All other treatments gave N_2 to N_2O ratios of between approximately 2.7 and 8.0. The ratio of 6.0 for the uncropped, h = -70 cm treatment is most likely not real due to the error in measuring very small fluxes. For very anoxic conditions it would be expected that the ratio would be large as is demonstrated by the large ratio of the manure plot compared to the other treatments. Without manure added to the plots the data show that there is still considerably more N_2 produced than N_2O.

Some N_2 and N_2O may have diffused below the 60 cm deep barrier of each plot and lost. The amount of gas lost in this manner was calculated from the N_2 and N_2O concentration gradient between the 30-and 60-cm depths and from the average gaseous diffusion coefficient between the two depths. Using a diffusion coefficient of 5 cm^2 hr^{-1} corresponding to a soil-air content of 0.12 (Rolston and Brown, 1977) the amount of N_2 and N_2O diffusion below the 60 cm depth was calculated to be 10, 5.5, and 2.5 kg N ha^{-1} for the manure, cropped, and uncropped plots, respectively, of the h = -15 cm water treatment.

TABLE 5. RATIOS OF N_2 TO N_2O PRODUCED FROM DENITRIFICATION IN THE PLOTS OF THE SUMMER EXPERIMENT FROM MEASUREMENTS BENEATH A COVER PLACED OVER THE SOIL

Treatment	N_2/N_2O ratio											Average N_2/N_2O ratio
	Days after NO_3^- application											
	0.25	1	2	3	4	5	6	7	8	10	13	
Manure, h = -15 cm	8.8	8.3	16.4	----	---	22.5	---	----	---	----	----	20.0
Manure, h = -70 cm	2.9	4.7	2.9	40.4	---	----	---	----	---	----	----	7.8
Cropped, h = -15 cm	2.8	4.3	1.9	2.2	---	----	7.0	----	8.9	14.6	17.7	7.0
Cropped, h = -70 cm	---	0.5	----	5.0	---	----	6.0	----	---	----	----	3.9
Uncropped, h = -15 cm	---	8.2	3.7	----	2.8	----	---	14.3	---	----	----	2.7
Uncropped, h = -70 cm	1.5	13.1	----	----	---	----	---	9.4	---	----	----	6.0

The concentration gradients for the 30- to 60-cm depth in the plots of the h = -70 cm treatment were very near zero so the loss of gas below the barrier was negligible.

Soil gaseous diffusion coefficients, determined by the CO_2 flux method, are given for four plots of the high-temperature experiment in Table 6. The

TABLE 6. SOIL GASEOUS DIFFUSION COEFFICIENTS DETERMINED BY THE CO_2 FLUX METHOD FOR THE SUMMER EXPERIMENT

Treatment	Date	D_p (cm^2 hr^{-1})
Manure, h = -15 cm	8/26	0.09
	9/16	0.009
	9/22	0.02
	10/6	0.05
Manure, h = -70 cm	10/7	1.02
	10/14	0.84
Uncropped, h = -15 cm	9/3	0.10
	9/21	0.07
Uncropped, h = -70 cm	10/11	4.07
	10/5	1.70
	11/11	2.14

diffusion coefficient of the cropped plots could not be determined using the CO_2 flux method because of the sink for CO_2 in photosynthesis. Each value in the table is the individually determined value for several different days. The diffusion coefficients for any plot tended to decrease with time indicating that the soil surface was becoming less permeable to the diffusion of gas as more irrigation water was applied. Determinations of diffusion coefficients were made more than one month after denitrification experiments were conducted. Thus, it may be expected that the measured diffusion coefficients would have been smaller than those during the denitrification experiment. These measured diffusion coefficients were generally an order of magnitude smaller than those required to approximate the measured flux as determined from a cover placed over the soil surface. These results demonstrate the very dynamic nature of the soil-gas duffusion coefficient and the importance of the soil surface condition on the transport of water and gas across the soil-atmosphere boundary.

Soil gaseous diffusion coefficients determined by the transient-state method (Equation 5) are given by Table 7. Values of D_p determined by the transient-state method are at least an order of magnitude larger than those determined by the steady-state method. The soil-air content, ε, is required to convert fitted values of D_m from the transient-state method to values of D_p. If only a portion of the total air space of the soil was contributing to diffusion as would occur with trapped air isolated by water films, the effective ε for diffusion would be much less than the total air space. Apparently,

TABLE 7. SOIL GASEOUS DIFFUSION COEFFICIENTS DETERMINED BY THE TRANSIENT-STATE METHOD FOR THE SUMMER EXPERIMENT

treatment	Date	D_m(cm^2 hr^{-1})	ε(cm^3 cm^{-3})	D_p(cm^2 hr^{-1})
Manure, h = -15 cm	9/15	90	0.078	7.0
Manure, h = -70 cm	10/6	120	0.119	14.3
	10/15	110		13.1
Cropped, h = -15 cm	9/16	220	0.008	1.8
	9/21	200		1.6
Cropped, h = -70 cm	9/28	100	0.023	2.3
	10/12	60		1.4
Uncropped, h = -15 cm	6/28	60	0.071	4.3
	9/14	80		5.7
Uncropped, h = -70 cm	10/7	225	0.086	19.4
	10/14	240		20.6
	11/9	200		17.2
	11/10	280		24.1

the effective ε must be less than 10% of the actually measured values of ε at the water contents maintained in the field plots.

Gas sampling within the soil profiles demonstrated that considerable $^{15}N_2$ was produced from denitrification of $^{15}NO_3^-$ fertilizer. Similar profiles were also measured for N_2O. For all plots except the manure plot at h = -15 cm, the $^{15}N_2$ concentrations were nearly constant with depth or decreased gradually near the surface. For the manure (h = -15 cm) treatment, however, the greatest concentrations of $^{15}N_2$ and N_2O were measured at the shallowest sampling depth of 2 cm. Thus, considerable denitrification occurred very near the soil surface. The largest denitrification rates generally occurred within 6 to 24 hours after applying NO_3^-. For the relatively high soil temperatures at which these experiments were conducted, denitrification began very quickly with large initial rates. The generally rapid decrease in denitrification with time was due to decreasing NO_3^- concentrations in soil solution and the displacement of NO_3^- into less anoxic zones. Considerable O_2 could be measured from samples taken within zones where denitrification was occurring. Thus, there must have been sites or "pockets" within the soil which were anoxic due to high microbial activity and small O_2 diffusion. In general, the greatest anoxic development occurs in the upper 30 to 60 cm of this profile (Rolston et al., 1976).

The addition of manure to the soil greatly increased the rate and total denitrification. The addition of crop residues would also increase the denitrification potential. The presence of living plants greatly increased the amount of denitrification as shown by the differences in N_2 and N_2O flux at the soil surface of the cropped and uncropped plots. The consumption of O_2 through respiration of grass roots and addition of carbon to the system from sloughed roots increased denitrification by approximately three to four times over that of the uncropped plots at equal soil-water pressures. For the uncropped plot maintained at a soil-water pressure head of -15 cm, only 8 kg of N ha^{-1} were lost as N_2 and N_2O. Thus, it appears that very little denitrification of added NO_3^- will occur from uncropped Yolo loam even under the most adverse soil-water conditions. The maximum rate of denitrification in the cropped plot maintained at h = -15 cm was considerably less than that reported by Rolston et al. (1976). The field plot used by Rolston et al. (1976) had been cropped with perennial ryegrass for approximately two years before application of NO_3^-, and the soil may have been slightly wetter than that of this study since water was occasionally pulled into the soil atmosphere samplers. It appears that long-term cropping with grass may substantially increase the available carbon of the soil and the denitrification potential.

The soil-water pressure also has a large effect on denitrification. By decreasing the soil-water pressure head from -15 to -70 cm, denitrification in the manure plots was decreased from 208 kg N ha^{-1} to 47 kg N ha^{-1}. Decreasing the soil-water pressure head from -15 to -70 cm for the cropped plots decreased total denitrification from 34 to 9 kg N ha^{-1}. Decreasing soil-water pressure in the uncropped plots decreased denitrification from 8 to 4 kg N ha^{-1}. The very narrow range of soil-water pressure for which denitrification occurs for this particular soil indicates that slight manipulation of soil-water content may be achieved to either increase or decrease denitrification depending upon particular objectives.

Plant Uptake

Figure 20 gives the cumulative N uptake by the grass as a function of time after the fertilizer was applied to the two cropped plots of the high-temperature experiment. The grass of the h = -70 cm treatment took up 20% of the applied fertilizer as compared to 11% uptake by the grass of the h = -15 cm treatment. This difference in uptake was due to the greater N loss through denitrification and the greater rate of N movement through the root zone of the h = -15 cm treatment. The rate of N uptake for both treatments was very large soon after the fertilizer was applied. The rate of N uptake in the h = -70 cm treatment also increased drastically at approximately 50 days after fertilizer was applied. This increase in N uptake was primarily due to increased dry matter production most likely due to decreasing air and soil temperature. The N uptake of the h = -15 cm treatment, however, did not increase at 50 days as did that of the h = -70 cm treatment since the fertilizer NO_3^- had been either denitrified or leached from the root zone by that time. Both plots had approximately the same rate of N uptake for the first 50 days.

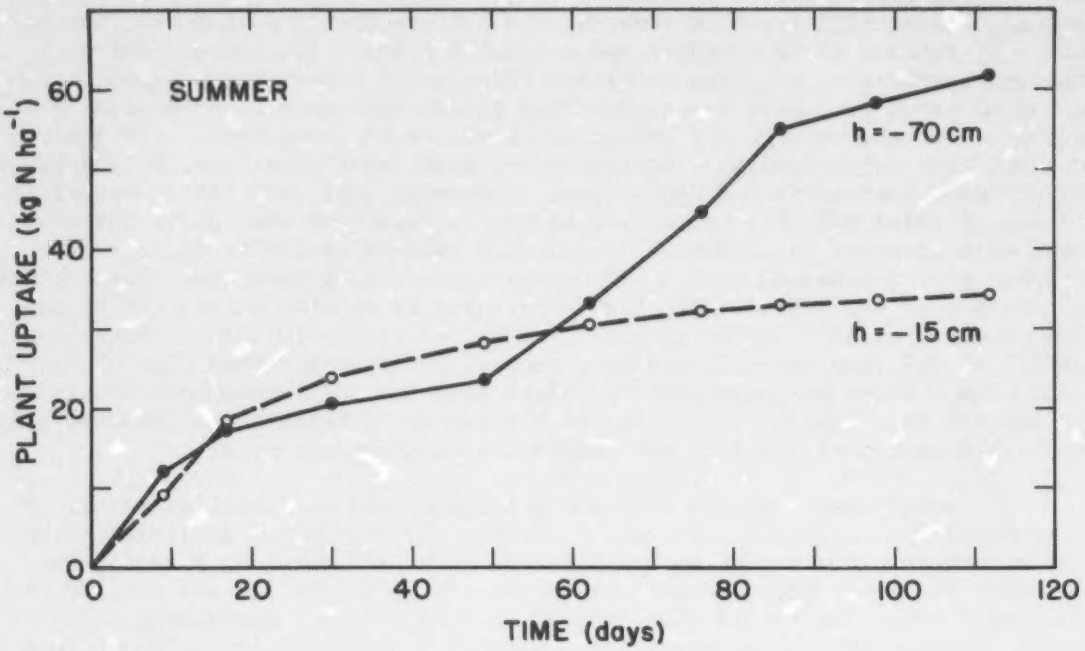

Figure 20. Plant uptake of fertilizer N with time of the summer experiment.

Leaching

Figure 21 gives soil solution NO_3^- concentrations derived from the fertilizer as a function of soil depth at approximately 125 days after application of the fertilizer to the h = -15 cm treatments. The large differences in denitrification among the cropped, manure, and uncropped plots of the h = -15 cm treatment also resulted in large differences in the concentration of fertilizer NO_3^- in the soil solution of the profile. As expected, the manure plot with the largest amount of denitrification resulted in the smallest NO_3^- concentrations in the soil solution. Denitrification in the uncropped plot of only 3% resulted in the largest NO_3^- concentration in the soil solution. The peak of the NO_3^- pulse for all three plots of the h = -15 cm treatment was at approximately 140 cm for 120 days after fertilizer application. On the other hand, for the h = -70 cm treatments, most of the NO_3^- was still in the upper 60 cm of the soil profile. An estimate of evapotranspiration was obtained from the water application rate for the h = -15 cm treatments, the volumetric water content of the soil profile, and the rate of movement of NO_3^- through the soil profile. Inasmuch as the profiles were kept constantly wet,

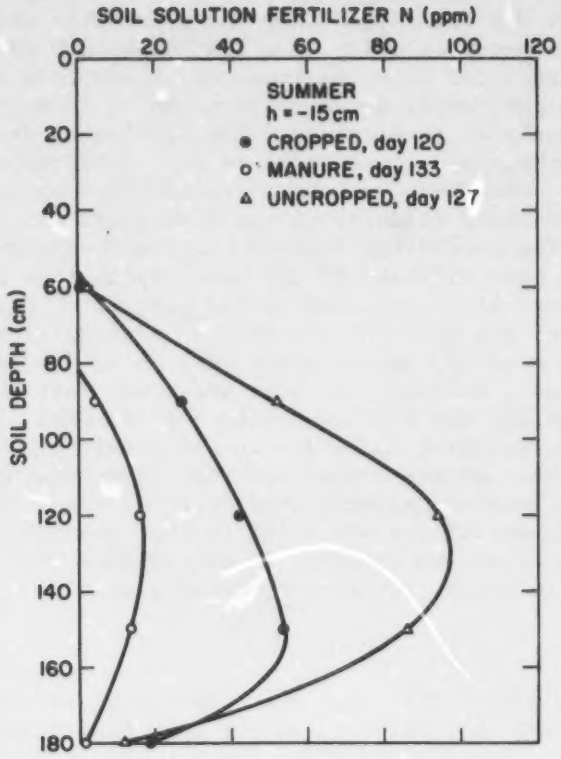

Figure 21. Concentration of fertilizer derived NO_3^- in the soil solution as a function of soil depth for the h = -15 cm treatments of the summer experiment.

it would be expected that evapotranspiration would be similar for all plots. Applying this estimated evapotranspiration to the h = -70 cm treatments gave a pore-water velocity, v_s, for the h = -70 cm treatments of approximately 0.5 cm day^{-1} as compared to 1.1 cm day^{-1} for the h = -15 cm treatments. From these estimates of pore-water velocity, the peak of the NO_3^- pulse should have been at about 55 cm at 110 days for the h = -70 cm treatment. Soil solution samples taken at 110 days show a slight increase in NO_3^- concentration at the 60 cm depth of the h = -70 cm treatments. The position of the NO_3^- pulse in the h = -70 cm treatments can be ascertained from the soil samples taken approximately 5.5 months after the NO_3^- was applied. The residual soil N will be presented in a later section.

The total leaching of NO_3^- from the h = -15 cm treatments was determined from the flux of water and the NO_3^- concentration at each of the 15 soil solution samplers as NO_3^- moved through the soil profile. The soil-water flux was

determined from the time of arrival of the NO_3^- peak at each sampler and the average water content above that sampler. The soil-water flux used in calculating NO_3^- recovery was determined from the pore-water velocity at each sampler, the mean pore-water velocity from the 9 samplers (3 plots) at each depth, the mean pore-water velocity from the 15 samplers of all depths of one plot, and the mean pore-water velocity from the 43 (2 samplers not functional) samplers of all depths of three plots. The results of determining NO_3^- recovery by these methods are given in Table 8. In calculating the NO_3^- leaching component, the mean recovery was calculated from all depths of each plot using the mean pore-water velocity of the 9 samplers at each depth (second row of Table 8). The pore-water velocity of the 9 samplers at each depth was considered the best estimate of the velocity at that depth inasmuch as velocity would change with depth due to changing water content with depth. Although this method was selected due to the above mentioned reason, the recovery percentages of any of the other methods of determining pore-water velocity are similar. However, the data indicate that the recovery percentages are too large for the shallow depths and too small for the deep depths. This discrepancy is believed to be due to the inability to accurately determine the water content at all depths and time from soil-water characteristic curves, limited soil-water pressure head data for the deeper depths, and nonuniform displacement of the NO_3^- pulse through the soil. These data demonstrate the difficulty and uncertainty in determining the leaching of NO_3^- in a field soil even in small, well-instrumented plots.

Residual Soil N

The extractable soil N derived from the fertilizer as a function of soil depth for the h = -70 cm treatments of the high-temperature experiment is given in Figure 22. Extractable N for the h = -15 cm treatments was very small. Extractable soil N includes NH_4^+, NO_2^-, and NO_3^- in solution and NH_4^+ on the exchange sites of the soil. The concentration of NH_4^+ was determined separately and found to be less than 1 ppm (usually smaller than 0.6 ppm in top 15-cm and much less below). The data points are mean concentrations within 15-cm depth increments from eight samples. The extractable N in the h = -70 cm treatments was large in the upper 60 cm of soil due primarily to NO_3^- which had not yet been leached out of the upper part of the profile.

The digestible soil N derived from the fertilizer as a function of soil depth for the six plots of the high-temperature experiment is given in Figure 23. Digestible soil N is that portion of the soil N existing as live or dead plant roots, microbial biomass, and fixed NH_4^+. Fixed NH_4^+ is expected to be small for Yolo loam soil. The data points are mean concentrations within 15-cm depth increments from eight samples. Digestible soil N was greatest near the surface due to plant roots and microorganisms. The cropped and manure plots resulted in the greatest digestible N, although the uncropped plots also had digestible N in the upper part of the profile. Digestible N in the manure and uncropped plots was due in part to microbial immobilization, although it was difficult to keep small weeds and moss from growing on the manure and uncropped plots which would immobilize N in roots. Although the manure plots had very little plant growth, considerable N was immobilized.

TABLE 8. PERCENTAGE RECOVERY OF FERTILIZER N LEACHED IN THE h = -15 CM PLOTS OF THE SUMMER EXPERIMENT CALCULATED BY VARIOUS WAYS OF DETERMINING THE SOIL-WATER VELOCITY, v_s. THE MEAN RECOVERY OF ALL DEPTHS FOR EACH PLOT IS GIVEN IN PARENTHESES

Method of determining pore-water velocity	% Recovery														
	Cropped					Manure					Uncropped				
	60	90	120	150	180	60	90	120	150	180	60	90	120	150	180
From v_s of each sampler	132	57	68 (72.4)	61	44	11	14	12 (11.6)	11	10	104	121	78 (85.0)	66	56
From mean v_s of all samplers at each depth (9 samples)	75	55	64 (59.0)	57	44	14	14	12 (12.4)	12	10	100	114	76 (82.6)	66	57
From mean v_s of all depths of one plot (15 samples)	86	64	68 (63.8)	57	44	13	14	11 (11.4)	10	9	110	129	77 (87.2)	65	55
From mean v_s of all depths of 3 plots (43 samples)	80	60	63 (59.4)	53	41	14	15	12 (12.2)	11	9	108	122	76 (84.4)	62	54

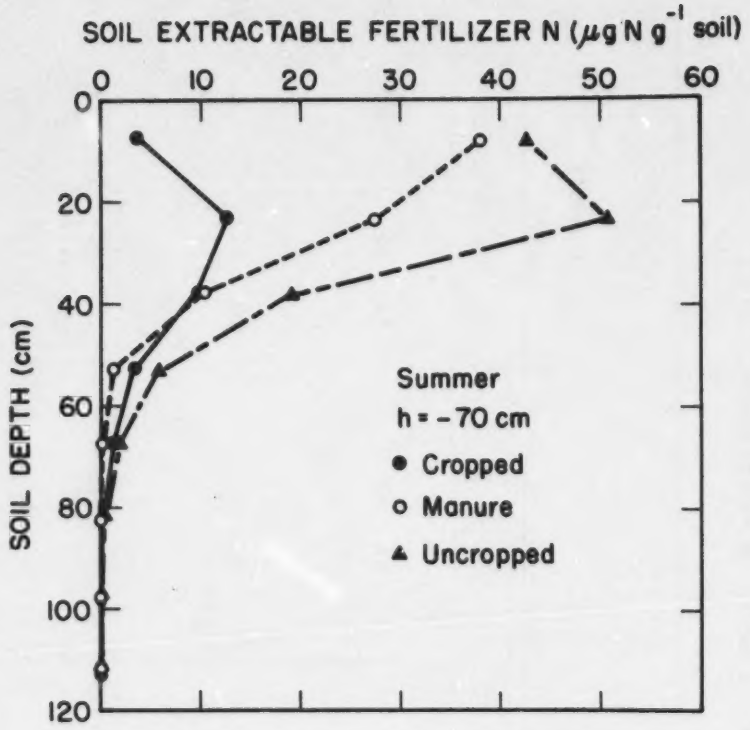

Figure 22. Soil extractable N from fertilizer as a function of soil depth, 5.5 months after fertilizer application, of the summer experiment.

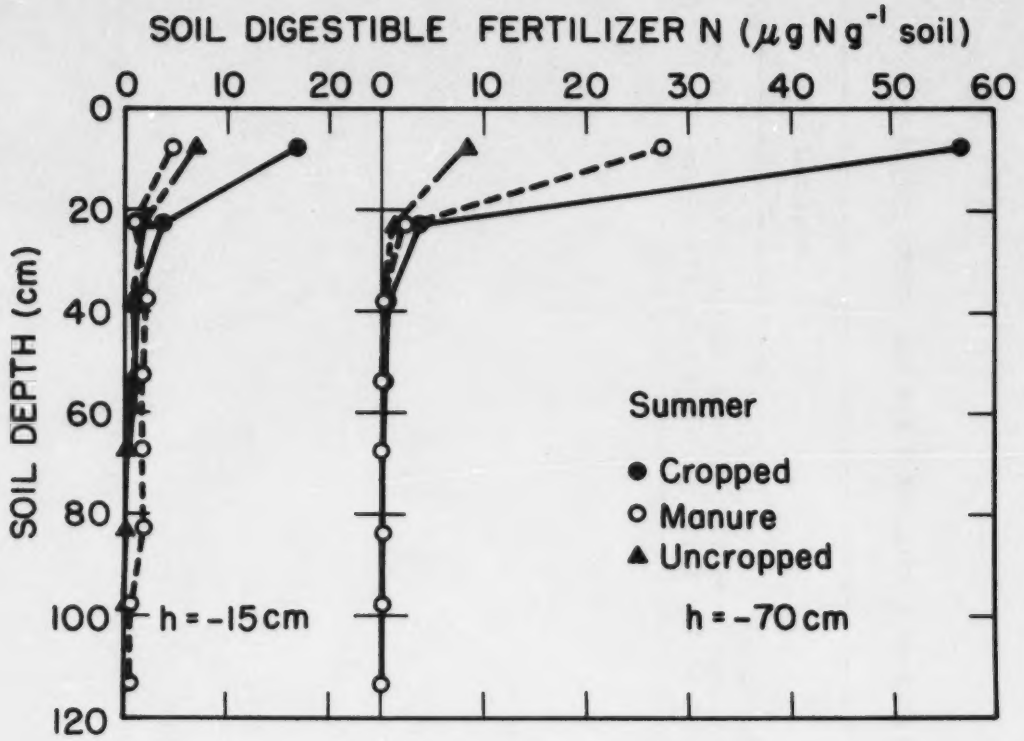

Figure 23. Soil digestible N from fertilizer as a function of soil depth, 5.5 months after fertilizer application of the summer experiment.

Mass Balance

Table 9 gives the N balance for each of the components of the N cycle. Denitrification was determined by difference from fertilizer application, plant uptake, leaching, and residual soil N. Denitrification as determined

TABLE 9. MASS BALANCE OF FERTILIZER N FOR THE SUMMER EXPERIMENT

Treatment	N_2O (kg N/ha)	N_2 (kg N/ha)	Gaseous loss below 60 cm (kg N/ha)	Leaching (kg N/ha)	Plant Uptake (kg N/ha)	Residual in soil		Denitrification	
						Extractable (kg N/ha)	Digestible (kg N/ha)	Direct (kg N/ha)	Difference (kg N/ha)
Manure, h = -15 cm	9.9	198	10	37	--	1	25	218	237
Manure, h = -75 cm	5.4	42	0	--	--	157	62	47	79
Cropped, h = -15 cm	4.3	30	5.5	175	34	0	52	40	35
Cropped, h = -75 cm	1.8	7	0	--	62	64	132	9	39
Uncropped, h = -15 cm	2.1	5.7	2.5	252	--	1	27	10	25
Uncropped, h = -75 cm	0.6	3.6	0	--	--	254	23	4	16

by difference is compared with denitrification determined from the flux of N_2 and N_2O at the soil surface and any gaseous loss below the 60-cm barrier. The amount of fertilizer applied to each plot is given by Table 2.

The direct method for determining denitrification compares reasonably well with the difference method. The direct method gave 19 kg N ha^{-1} less denitrification than did the difference method for the manure, h = -15 cm treatment. A difference of only 19 kg N ha^{-1} could easily be accounted for by an underestimation of the gaseous flux on hot afternoons since measurements were generally taken mid-morning, by small denitrification rates below the detection limits for $^{15}N_2$ over several weeks, and errors in measuring leaching and residual soil N. Denitrification calculated directly was slightly greater (5 kg N ha^{-1}) than that of the difference method for the cropped, h = -15 cm treatment. This difference may be explained by an overestimation of the leaching component since all samplers, including those at the 60-cm depth, were used in determining NO_3^- leaching. It would be expected that plant roots could take up some additional N below 60 cm and thus, result in an overestimation of the leaching.

For all other plots, denitrification as determined directly was between 12 and 30 kg N ha^{-1} less than that determined by difference. The substantial differences between the two methods for the h = -70 cm treatments may be explained by small rates of gaseous loss below the minimum detection limits over several weeks and elevated rates on hot afternoons which were not measured. These speculations seem especially reasonable since the NO_3^- pulse remained in the upper 60 cm of the profile for several months. There may also be some error in the residual soil N component of the difference method. The sensitivity of the direct method may be increased by increasing the ^{15}N enrichment of the added fertilizer, increasing the time that covers remain over the soil surface, decreasing the volume of the chamber placed over the soil surface, or by calculating gas flux from diffusion coefficients and concentration gradients within the soil. Although larger concentrations are possible from soil air samples, the latter method is plagued with uncertainty in measuring both the diffusion coefficient and the concentration gradient (Rolston, 1977).

LOW-TEMPERATURE EXPERIMENT

Plot Characteristics

Temperature at the 5-cm soil depth as a function of time after fertilizer was applied to the plots of the winter experiment is given by Figure 24. The average soil temperature during most of the denitrification activity was approximately 8-10°C. There was a gradual increase in soil temperature approximately two weeks after the fertilizer was applied to the first plot. The labeled arrows in the figure give the fertilizer applications to each of the six plots. The fertilizer was applied to plots at a temperature of 8-10° C except for the cropped plot of the dry treatment at which the temperature was 10-13°C.

The soil-water pressure head, h, for the 5- and 15-cm depths as a function of time after fertilizer application for the winter experiment is given by

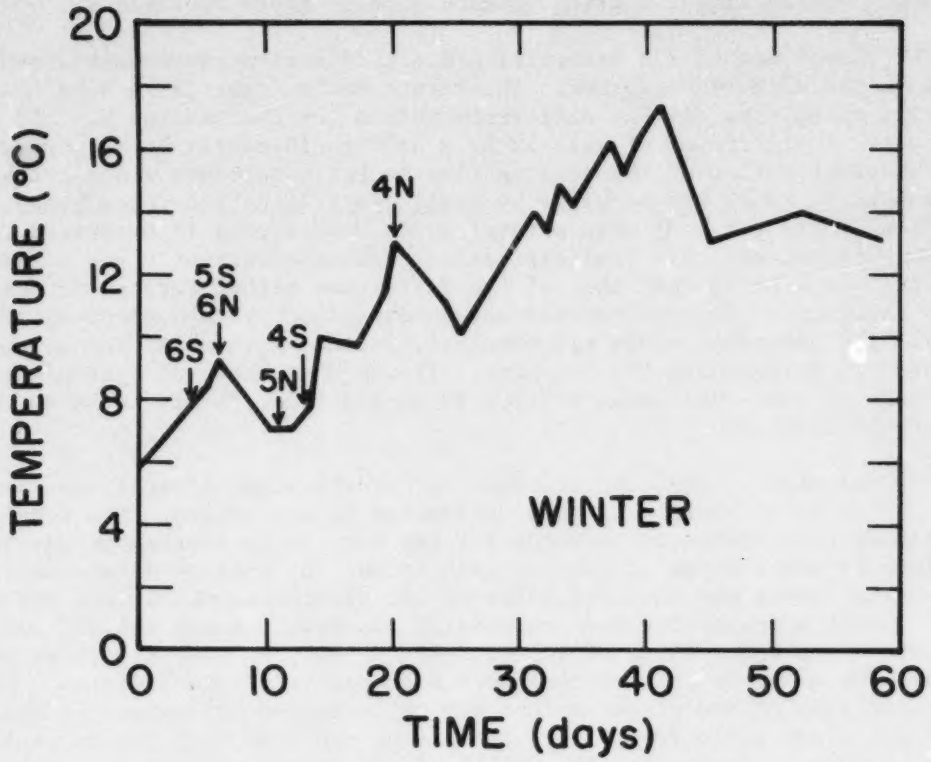

Figure 24. Mean soil temperature at the 5-cm soil depth as a function of time after fertilizer was applied to the plots of the winter experiment. The arrows give the fertilizer application for each plot with the symbols given in Table 2.

Figure 25. The soil-water pressures during the fertilizer application were approximately -6 to -8 cm for the wet treatment, and approximately -50 cm for the dry treatment. The arrows in the figure give the times that the fertilizer was applied to each plot. The pressure heads are mean values of the three plots of each soil-water treatment. Values of the soil-water pressure head as a function of depth are given by Figure 26. As with the summer experiments, the soil-water pressure heads became smaller with depth. In a similar manner, the soil-water content data as a function of depth for the two water treatments are given in Figure 27. These data were obtained from neutron moisture probe data, and the data points are mean values for the three plots of each water treatment. Water contents determined from neutron meter data compare closely with those from tensiometers and soil-water characteristic curves. The soil-air content, ε, as a function of depth can be calculated and is plotted in Figure 28 for the two soil-water treatments. These values

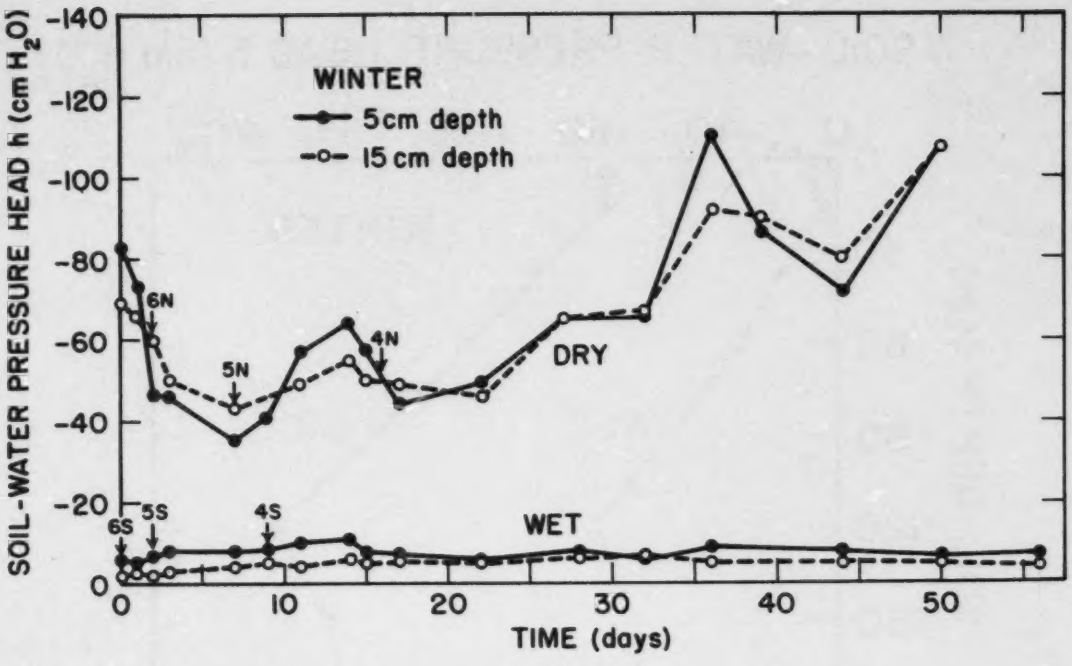

Figure 25. Mean soil-water pressure head at the 5- and 15-cm soil depth as a function of time after fertilizer application to the two water treatments of the winter experiment. The arrows give the fertilizer application for each plot.

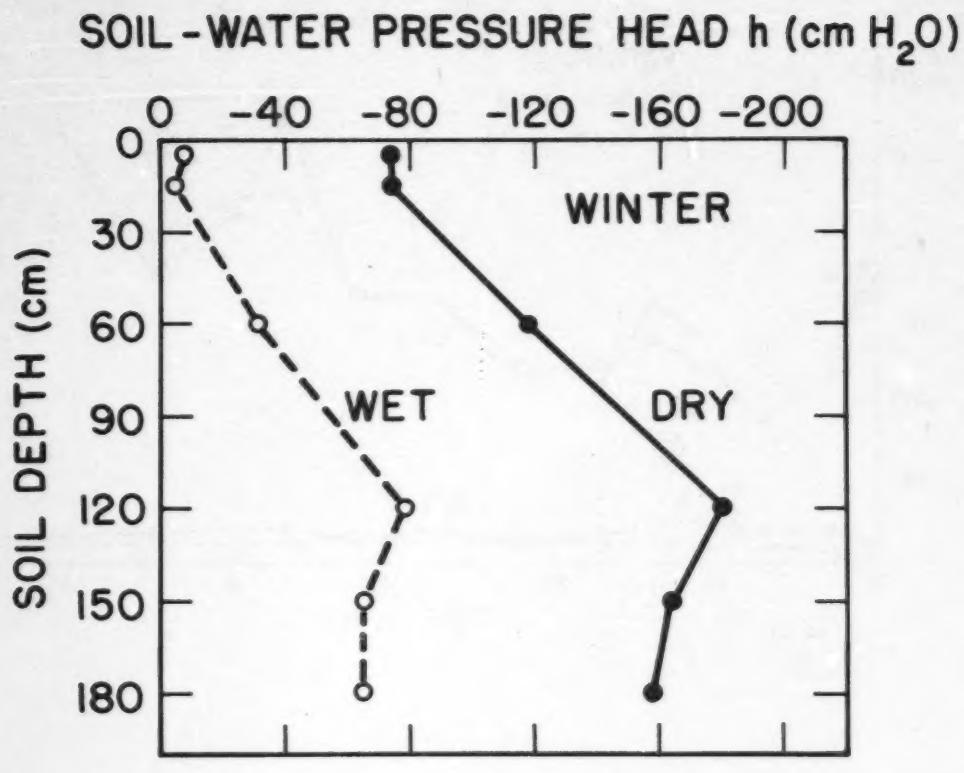

Figure 26. Mean soil-water pressure head as a function of soil depth for the two water treatments of the winter experiment.

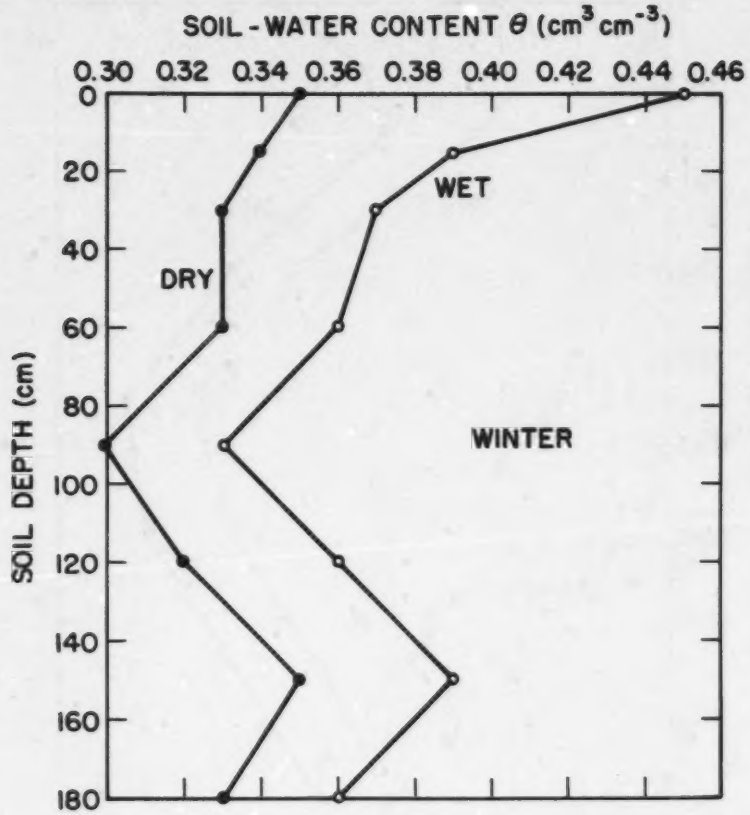

Figure 27. Mean soil-water content as a function of soil depth for the two water treatments of the winter experiment.

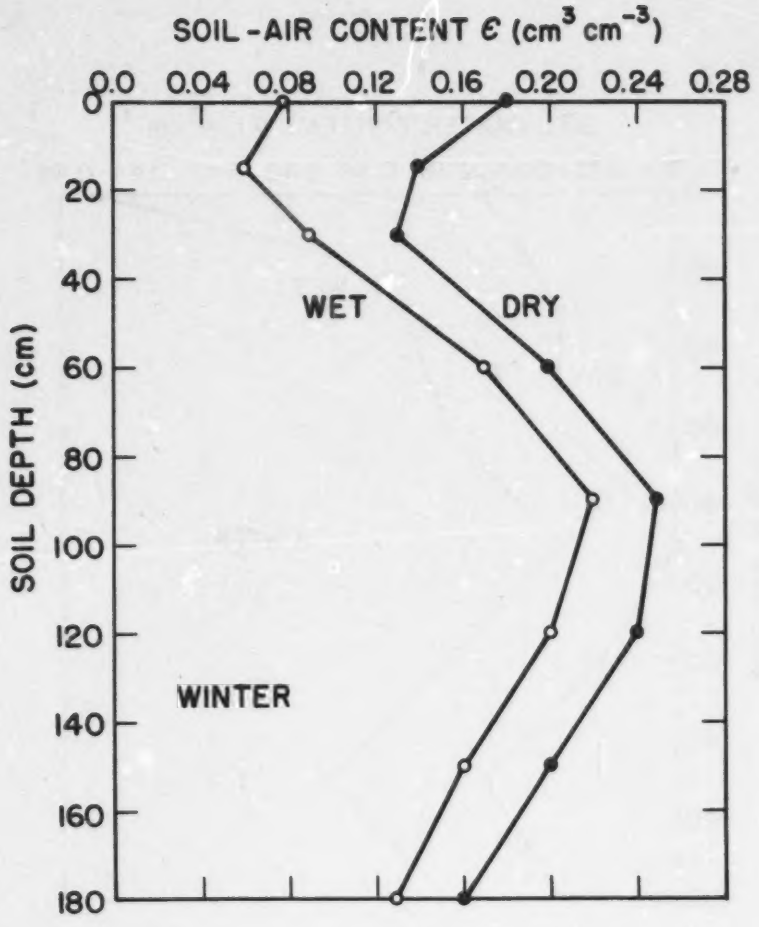

Figure 28. Mean soil-air content as a function of soil depth for the two water treatments of the winter experiment.

of ε are average values for the three plots of each water treatment. The h = -8 cm and h = -50 cm treatments result in only very small differences of soil-air content in the surface soil.

Soil Gases

The amount of O_2 in the soil as a function of soil depth for the six plots of the winter experiment is given by Figure 29. The O_2 concentrations

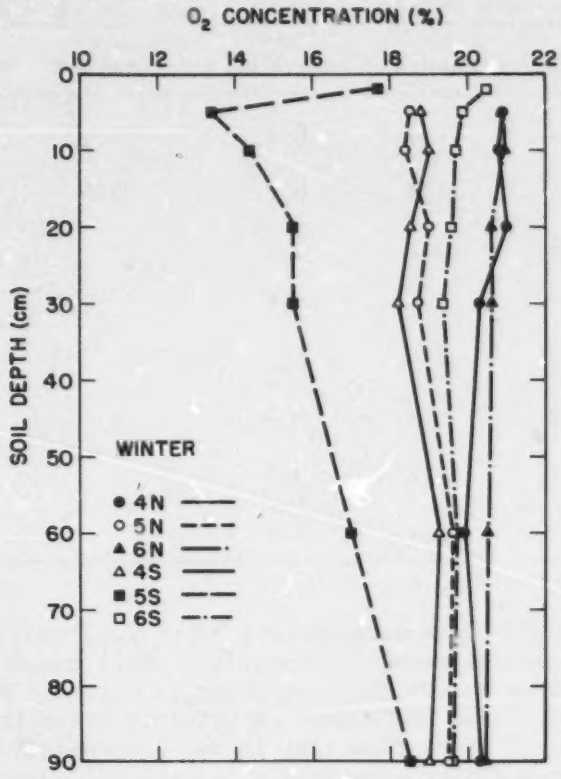

Figure 29. Oxygen concentration as a function of soil depth in the plots of the winter experiment. The symbols are given in Table 2.

were measured during the time that the denitrification experiments were conducted. Because of decreased biological activity at low temperature, all plots exhibited relatively uniform O_2 concentrations with depth. The only major deviation among plots was the manure, h = -8 cm treatment. The minimum value attained in that particular plot was approximately 13% at the 5-cm depth. All other plots had O_2 values between 18 and 21%. Although O_2 concentration within the profile gave only a qualitative estimate of anoxic development, it is obvious from Figure 29 that anoxic development in the profiles was smaller than those of the summer experiment.

The initial concentration of N_2O within the six plots of the winter experiment before application of NO_3^- fertilizer is given by Table 10. The

TABLE 10. CONCENTRATION OF N_2O (PPMV) WITHIN PROFILES BEFORE APPLICATION OF FERTILIZER OF THE WINTER EXPERIMENT. AMBIENT CONCENTRATION OF N_2O IN AIR IS APPROXIMATELY 0.30 PPMV

Soil Depth (cm)	h = -8 cm			h = -50 cm		
	Cropped	Manure	Uncropped	Cropped	Manure	Uncropped
2	0.6	11.0	0.7	0.5	19.0	0.5
5	0.6	12.8	0.7	0.5		0.5
10	0.6	15.1	0.6		18.0	0.5
15		15.6	0.8	0.6		0.5
20	0.8	8.5	1.1		11.8	0.6
30	0.7	6.9	0.7	1.0	8.0	0.7
60	2.1	2.2	0.7			0.8
90		1.4	0.8			0.8

N_2O concentrations in all plots were above ambient (0.3 ppm) indicating that conditions were not reduced enough to cause the small amount of N_2O produced to be further reduced to N_2. This observation is entirely different from that of the cropped plots of the summer experiments where the small amount of N_2O produced was reduced to N_2 resulting in N_2O concentrations below ambient. The manure plots of the winter experiments had initial concentrations of N_2O as large as 20 ppm. All other plots were slightly above the ambient concentration with very little difference between plots.

Representative N_2O concentration profiles from denitrification of added fertilizer as a function of soil depth at 7 days after fertilizer application for the h = -8 cm treatments are given by Figure 30. The concentration profiles demonstrate that considerable differences in N_2O production occurred among the cropped, manure, and uncropped plots, although the differences are not nearly as great as those observed during the summer experiments. Also, the N_2O concentration profiles were generally much smoother and uniform with depth than were those of the summer experiment. Similar data for the plots of the h = -50 cm treatment at 7 days after application of the fertilizer are shown by Figure 31. There was much less production of N_2O in the h = -50 cm treatments than in the h = -8 cm treatments, and the concentration profiles

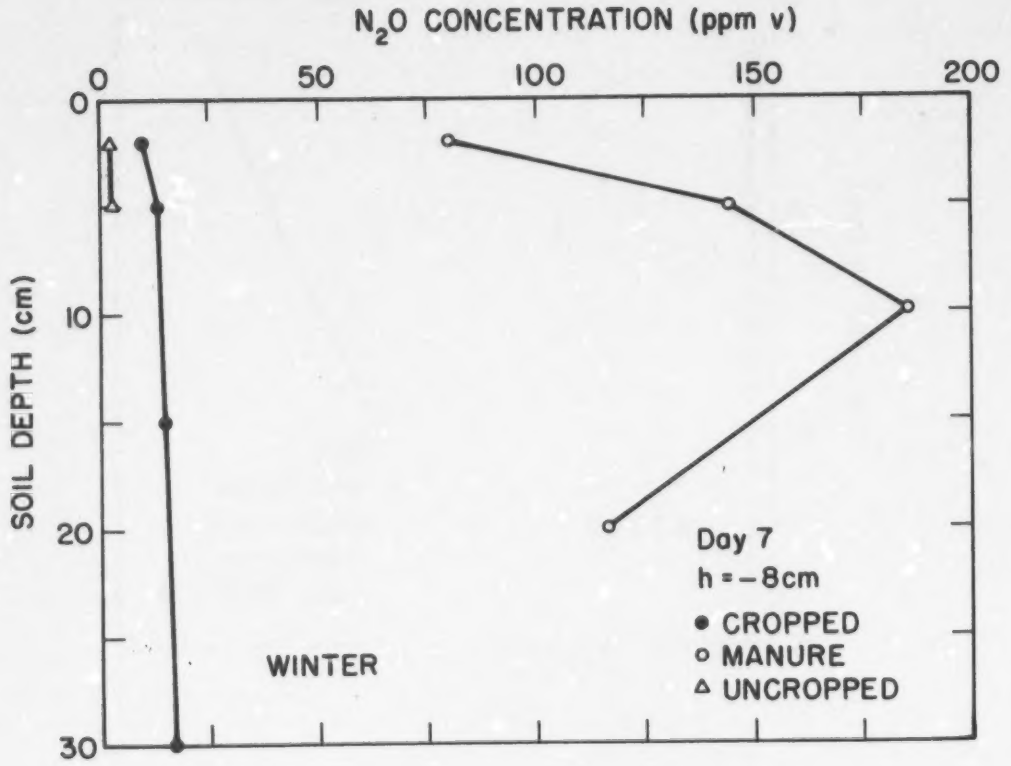

Figure 30. Nitrous oxide concentration with depth on one day in the h = -8 cm treatment of the winter experiment.

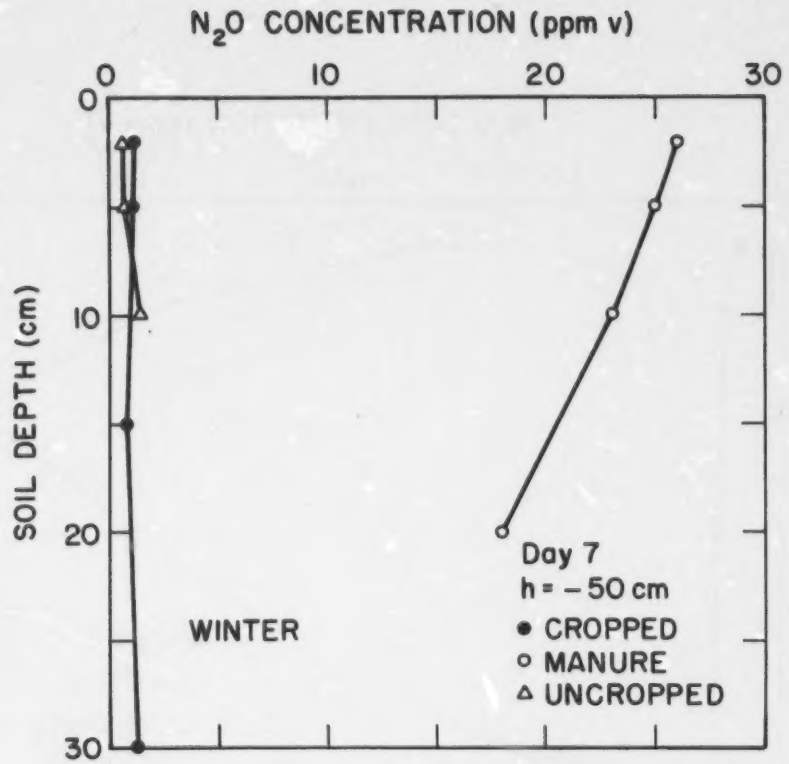

Figure 31. Nitrous oxide concentration with depth on one day in the h = -50 cm treatment of the winter experiment.

were fairly uniform with depth. The largest N_2O production occurred in both the h = -8 and -50 cm water treatments of plots to which manure had been added in the top 10 cm of soil.

Similar representative N_2 profiles derived from the fertilizer at 7 days after application of the fertilizer are given in Figures 32 and 33. Concentration profiles for $^{15}N_2$ gas follow the same pattern as that of N_2O with differences in N_2 production among the cropped, manure, and uncropped plots. However, substantial denitrification occurred only in the manure plots.

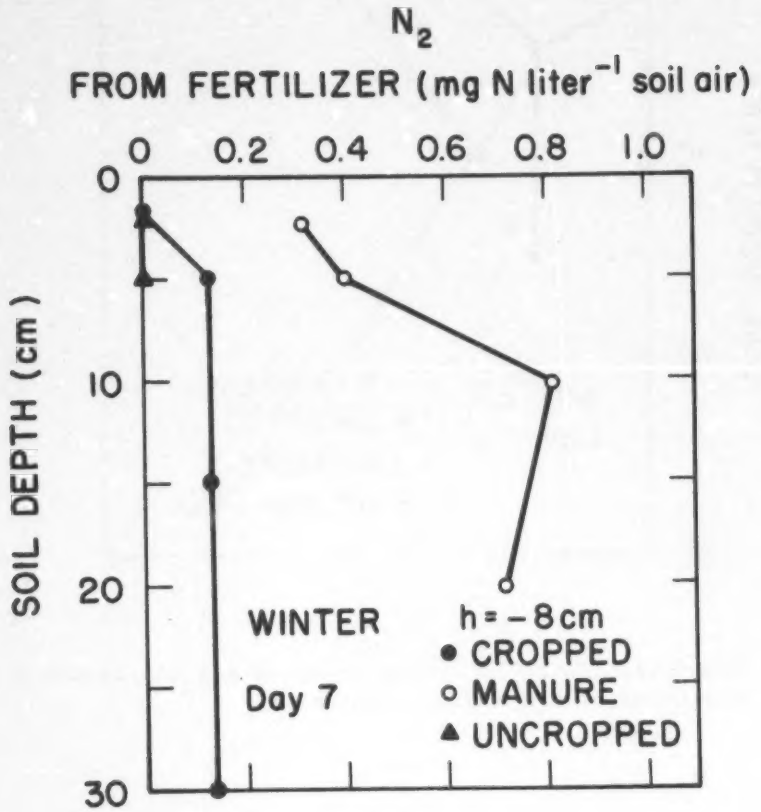

Figure 32. Concentration of $^{15}N_2$ with depth on one day in the h = -8 cm treatment of the winter experiment.

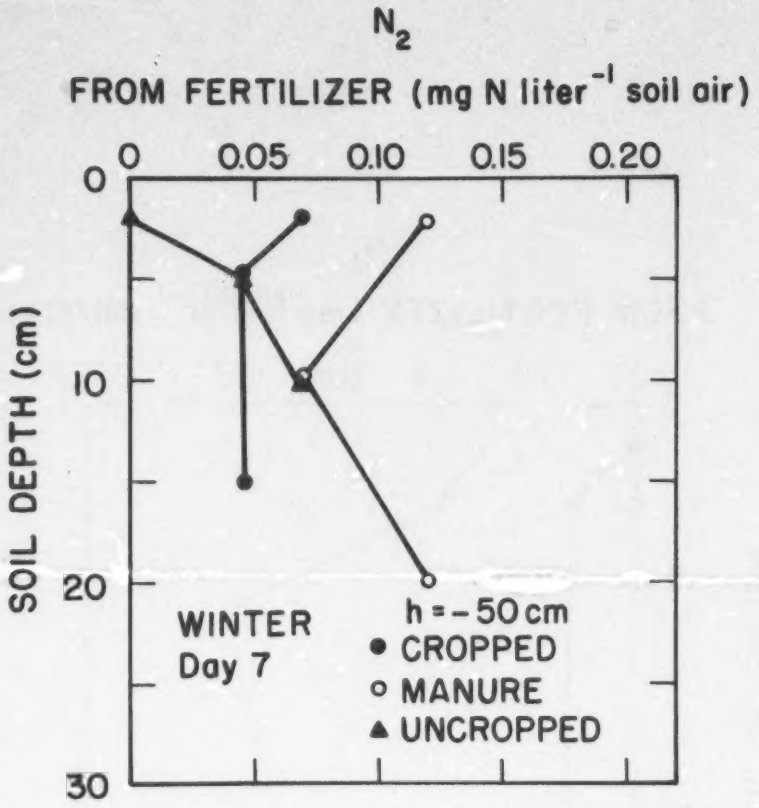

Figure 33. Concentration of $^{15}N_2$ with depth on one day in the h = -50 cm treatment of the winter experiment.

Gas Fluxes

Flux of N_2O derived from the fertilizer as a function of time for the manure and cropped plots is given by Figure 34. These fluxes were determined from the accumulation of N_2O beneath the cover placed over the soil surface for 1- or 2-hour intervals. The numbers below each of the soil-water pressure head treatments are total N_2O produced as determined from the area beneath each of the flux versus time curves. All data were corrected for the concentration increase beneath the cover using Equations (6), (7), and (8).

As with the N_2O flux data of the summer experiments, the flux of gases from denitrification occurred immediately after addition of the fertilizer. However, the N_2O flux increased at a much smaller rate than that of the summer experiments. In all cases the total amount of denitrification which occurred as N_2O was very small. Similar data from the flux of N_2O from the fertilizer as a function of time for the uncropped plots are given by Figure

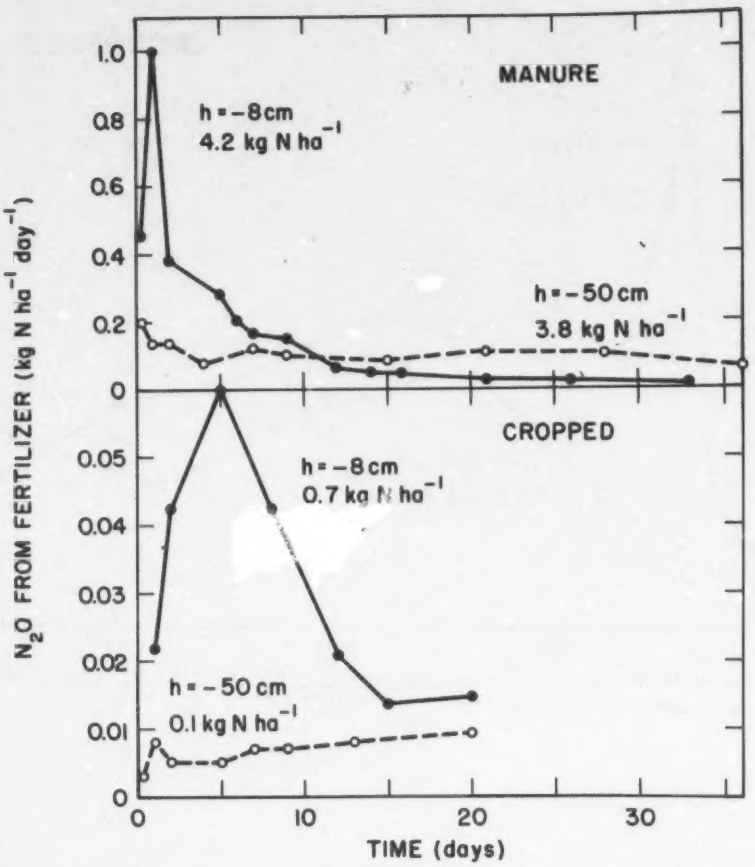

Figure 34. Flux of N_2O calculated from measurements beneath a cover with time for the manure and cropped plots of the winter experiment.

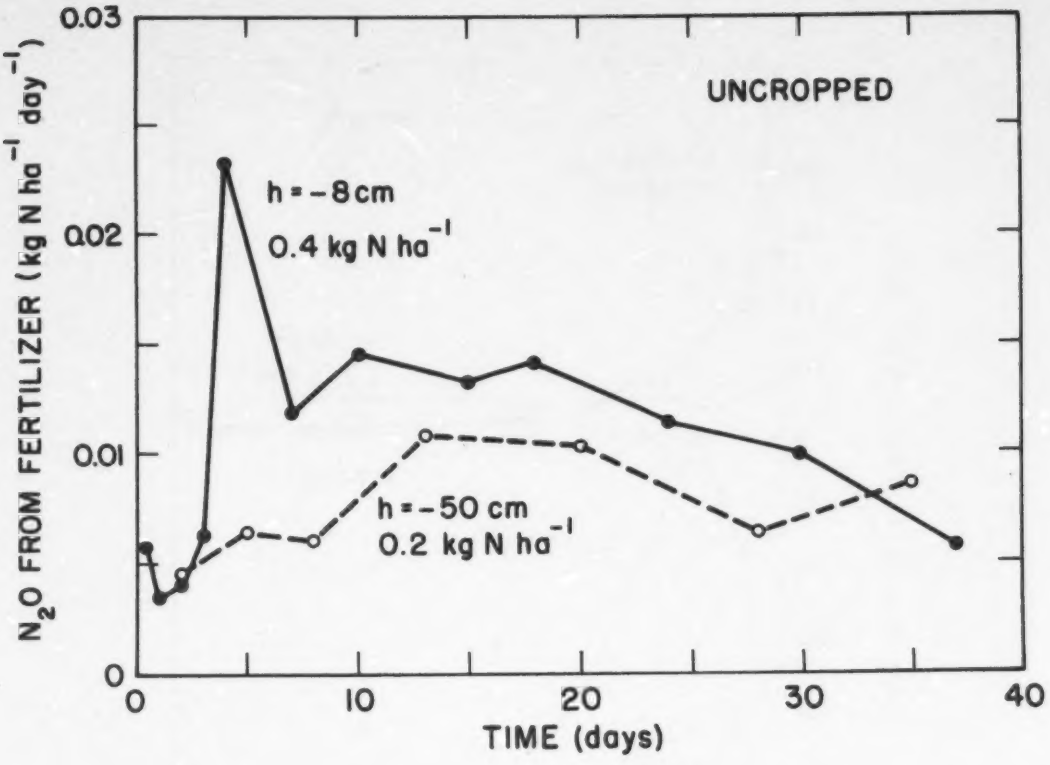

Figure 35. Flux of N_2O calculated from measurements beneath a cover with time for the uncropped plots of the winter experiment.

35. Again, very little denitrification as N_2O occurred in the uncropped plots with the total amount being only slightly different than that which occurred in the cropped plots. Denitrification occurred for a much longer time period than for the summer experiments, although concentrations and fluxes were small.

Data for the flux of N_2 derived from the fertilizer as a function of time for the manure and cropped plots are given by Figure 36. These fluxes

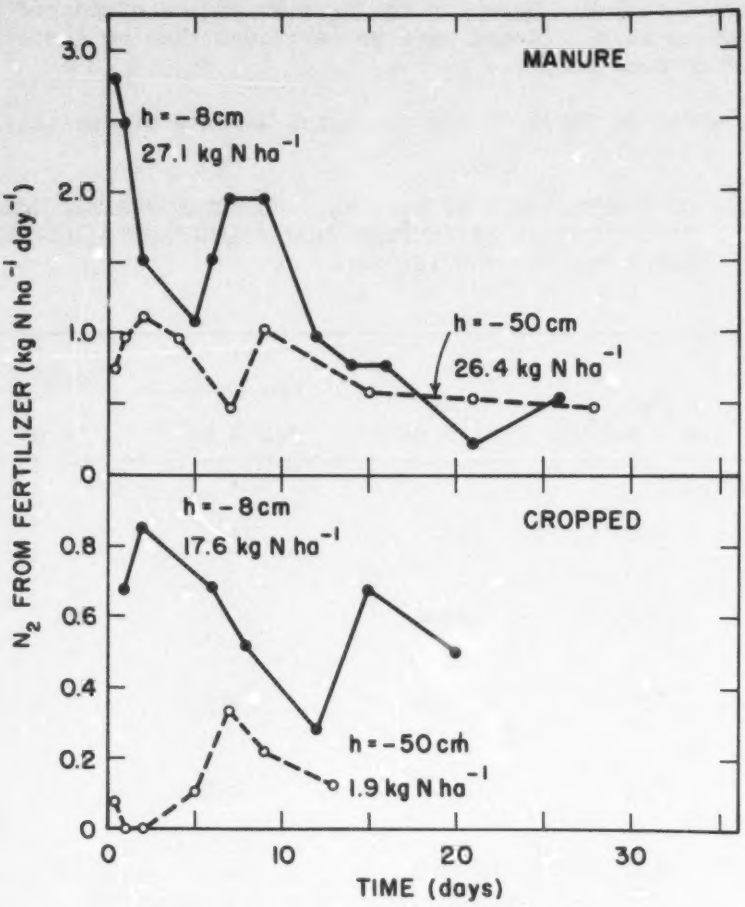

Figure 36. Flux of $^{15}N_2$ calculated from measurements beneath a cover with time for the manure and cropped plots of the winter experiment.

were determined from the accumulation of N_2 beneath the cover placed over the soil surface and corrected for the decrease in the concentration gradient as N_2 accumulated. The numbers below each of the soil-water pressure head treatments are total N_2 produced. Denitrification was largest soon after application of the fertilizer and decreased to relatively small values by approximately 20 days. As determined by the criterion used for measuring the N_2 beneath the cover over the soil, the minimum value which we considered significantly different than background or machine noise was approximately 1 kg N ha^{-1} day^{-1}. Thus, all of the N_2 fluxes given in Figure 36 except for the manure, h = -8 cm treatment were either at or below what is considered as the minimal detectable limit. Thus, the uncertainty of the denitrification in this very small flux range is quite large. There was very little difference in denitrification in the manure plots of the h = -8 and -50 cm treatments, although there was considerable uncertainty in the fluxes at these small

rates of denitrification. Data for the N_2 flux of the uncropped plots are not given inasmuch as all fluxes were so near zero that no denitrification was considered to have occurred as N_2.

The data given in Table 11 are the total amounts of denitrification

TABLE 11. DENITRIFICATION AS N_2O, N_2, AND TOTAL FOR THE WINTER EXPERIMENT AS DETERMINED FROM MEASUREMENTS BENEATH A COVER PLACED OVER THE SOIL

Treatment	N_2O (kg N ha^{-1})	N_2 (kg N ha^{-1})	Total (kg N ha^{-1})	Total (% of fertilizer)
Manure, h = -8 cm	4.2	27.1	31.3	11
Manure, h = -50 cm	3.8	26.4	30.2	10
Cropped, h = -8 cm	0.7	17.6	18.3	6
Cropped, h = -50 cm	0.1	1.9	2.0	1
Uncropped, h = -8 cm	0.4	0.0	0.4	≃ 0
Uncropped, h = -50 cm	0.2	0.0	0.4	≃ 0

consisting of both N_2 and N_2O for the six treatments of the winter experiment. The amount of denitrification ranged from zero for the uncropped plots to 11% of the total fertilizer added for the manure, h = -8 cm treatment. The water content or carbon level had very little influence on the total amount of denitrification at these low temperatures.

The N_2 to N_2O ratio as a function of time after application of the NO_3^- to each of the plots is given in Table 12. The average ratio calculated on the basis of total amount of each gas produced is also given. The largest ratios of 25 and 19 occurred for the cropped treatments at h = -8 and -50 cm, respectively. These ratios may be somewhat uncertain inasmuch as the flux of N_2 was below that flux considered to be significant.

Soil gaseous diffusion coefficients, determined by the CO_2 flux method, are given for four plots of the winter experiment in Table 13. Diffusion

TABLE 12. RATIOS OF N_2 TO N_2O PRODUCED FROM DENITRIFICATION IN THE PLOTS OF THE WINTER EXPERIMENT FROM MEASUREMENTS BENEATH A COVER PLACED OVER THE SOIL

Treatment	N_2/N_2O ratio								
	Days after NO_3^- application								
	0.25	1	2	4	5	6	7	8	9
Manure, h = -8 cm	6.2	2.5	3.8	---	4.3	7.5	11.9	---	12.7
Manure, h = -50 cm	3.8	6.9	8.2	12.9	---	---	4.0	---	10.0
Cropped, h = -8 cm	---	30.9	20.0	---	---	11.3	---	12.2	---
Cropped, h = -50 cm	25	---	---	---	20	---	48.6	---	31.4

TABLE 12 (continued)

Treatment	N_2/N_2O ratio								Average N_2/N_2O ratio
	Days after NO_3^- application								
	12	13	14	15	16	20	21	28	
Manure, h = -8 cm	15.8	---	15.0	---	18.8	---	---	---	6.5
Manure, h = -50 cm	---	---	---	6.8	---	---	4.8	4.8	6.9
Cropped, h = -8 cm	13.3	---	---	51.5	---	34.5	---	---	25.1
Cropped, h = -50 cm	---	16.2	---	---	---	---	---	---	19.0

TABLE 13. SOIL-GAS DIFFUSION COEFFICIENTS FOR THE WINTER EXPERIMENT

Treatment	Date	D_p(cm^2 hr^{-1})	Date of Fertilizer Application
Manure h = -8 cm	2/2	0.84	1/12
	4/5	0.40	
	4/14	0.24	
	4/15	0.10	
	4/28	0.25	
Manure h = -50 cm	3/10	2.43	1/17
	4/7	3.29	
	4/12	2.55	
Uncropped h = -8 cm	12/10	2.79	1/10
	12/15	1.59	
	12/17	1.56	
	2/3	0.44	
	5/16	0.30	
	5/17	0.41	
Uncropped h = -50 cm	11/9	5.40	1/12
	11/10	7.06	
	12/1	3.53	
	12/13	2.84	
	12/14	1.77	

coefficients for N_2 are approximately 1.25 times larger than those of CO_2. Each value in the table was determined on different days. Diffusion coefficients generally decreased with time in a similar manner to those of the summer experiments due to changing soil surface conditions. Diffusion coefficients were used in conjunction with measured N_2 and N_2O concentration gradients (five samplers at each depth) to calculate the denitrification flux from Equation (1). Values of the diffusion coefficients required in Equation (1) in order to result in the same amount of denitrification as determined

from beneath the cover were approximately equal to measured values of the h = -50 cm treatments (Table 13). For instance, a value of D_p equal to 4 cm^2 hr^{-1} for the h = -50 cm treatments resulted in the calculated flux to be equal to the measured gas flux. Values of D_p required in order that the calculated flux for the h = -8 cm treatments be equal to the measured flux were larger than those measured (Table 13). For instance, a value of D_p equal to approximately 2.7 cm^2 hr^{-1} for the h = -8 cm treatments resulted in the calculated flux to be equal to the measured flux from gas accumulation beneath covers. The underestimation of denitrification flux from Equation (1) was due primarily to the general decrease in diffusion coefficients with time and the resultant uncertainty in knowing the value of D_p during denitrification. However, additional gaseous transport mechanisms such as mass flow due to pressure fluctuations of a barometric and wind turbulence source cannot be absolutely neglected. The very dynamic nature of diffusion coefficients, strongly dependent upon surface soil conditions, requires that the measurement of D_p be made several times as close as possible to the time period of denitrification. Although the temporal variability of the gaseous diffusion coefficient results in some uncertainty in calculating flux of gases from denitrification, Equation (1) can be used to determine denitrification if accurate measurements of diffusion coefficients and concentration gradients are made. The advantage of calculating flux from Equation (1) over measuring flux from accumulation of gas beneath a cover is the increased sensitivity due to larger concentrations of $^{15}N_2$ within the soil than that from accumulation beneath a cover.

Measurements of $^{15}N_2$ and N_2O within the soil profiles and beneath the lids placed over the soil surface demonstrated that very little denitrification of added NO_3^- occurred at the low temperatures of approximately 8-10°C. However, there was some denitrification in the manure and cropped plots with rates being very small. The addition of manure to the soil greatly increased denitrification over that of the cropped plots. Low amounts of denitrification were due to low microbial activity which was reflected in relatively constant and high values of O_2 within the soil profile. Differences in denitrification due to soil-water treatment were not great due to the overall small rates of denitrification and uncertainty in the measured fluxes at small denitrification rates.

Plant Uptake

Figure 37 gives the cumulative N uptake by the grass as a function of time after the fertilizer was applied to the two cropped plots of the winter experiment. The grass of the h = -50 cm treatment took up 47% of the applied fertilizer at 115 days after application compared to 35% for the h = -8 cm treatment. The rate of N uptake was similar for both treatments until approximately 50 days after application, at which time the NO_3^- pulse was being leached below the major root zone in the h = -8 cm treatment. The N uptake was much greater for the grass of the winter experiment than that of the summer experiment. The difference in uptake was due to a much greater dry matter production during the winter than in the summer because of more favorable growing conditions.

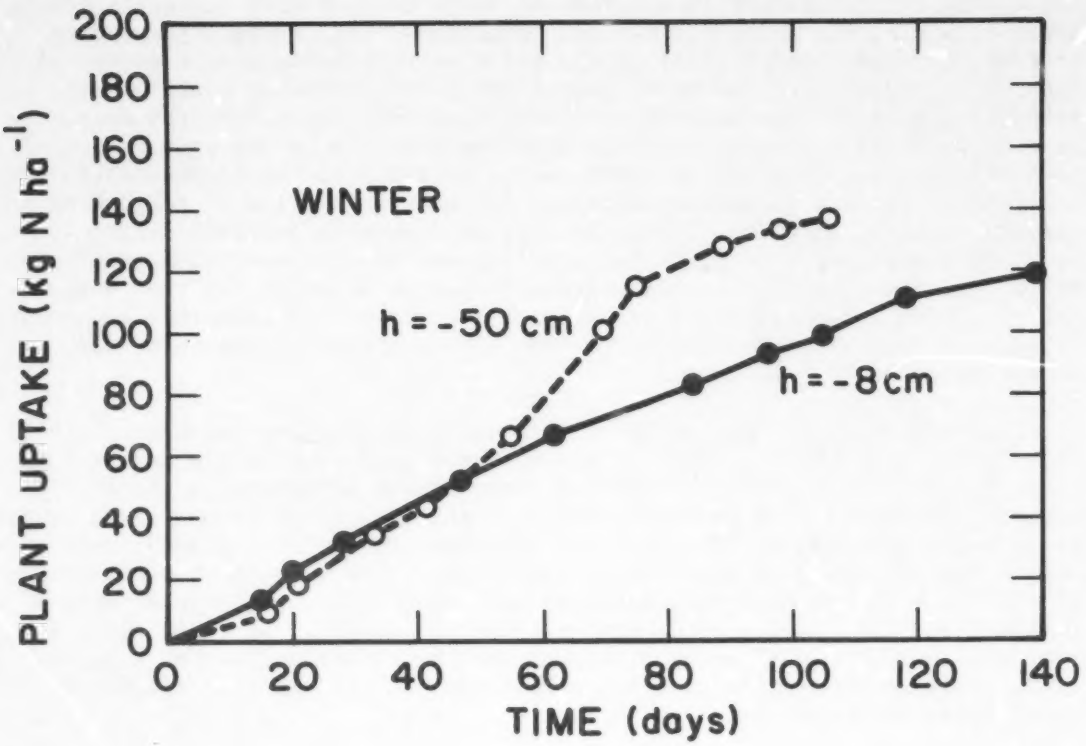

Figure 37. Plant uptake of fertilizer N with time during the winter experiment.

Leaching

Figure 38 gives soil solution NO_3^- concentrations derived from the ferti-

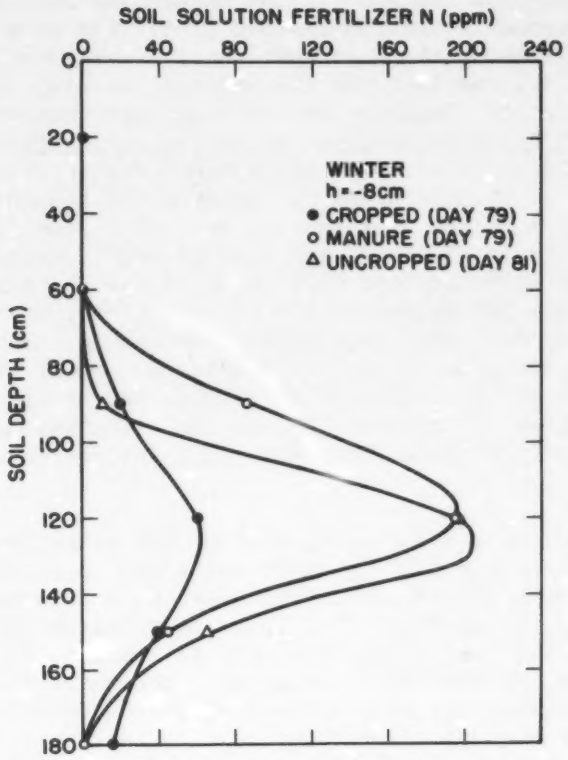

Figure 38. Concentration of fertilizer derived NO_3^- in the soil solution as a function of soil depth for the h = -8 cm treatments of the winter experiment.

lizer as a function of soil depth at approximately 80 days after application of the fertilizer to the h = -8 cm treatments. Since denitrification was small for all three plots, the greatest difference in the leaching component was due to the large plant uptake. Thus, the NO_3^- concentrations in the cropped plot were much less than in either the manure or the uncropped plots. The NO_3^- pulse moved faster through the plots of the winter experiment than through those of the summer experiment.

The total leaching of NO_3^- from the h = -8 cm treatments was determined from the flux of water and the NO_3^- concentration at each of the 15 soil solution samples of each plot using the same approach as described for the summer

experiments. The recovery percentages using various ways of averaging the soil-water velocity are given in Table 14. The NO_3^- leaching component was calculated using the mean soil-water velocity of the 9 samplers at each depth since the soil-water velocity tended to change slightly with depth. All approaches for averaging the soil-water velocity resulted in recovery of much more fertilizer N than was applied for the manure and uncropped treatments and more than is reasonable for the cropped plot. The mean recovery determined from all depths using the mean soil-water velocity of the 9 samplers at each depth was 56, 138, and 182% for the cropped, manure, and uncropped plots, respectively. The greater recovery as leaching than that applied as fertilizer may be explained by an overestimation of the soil-water velocity or flux of water in the field profiles. The average soil-water flux ($v_s\,\theta$) was calculated from values of v_s determined by the time the NO_3^- peak reached a particular depth. Values of the flux for the 60-, 90-, 120-, 150-, and 180-cm depths were 0.54, 0.58, 0.55, 0.52, and 0.49 cm day^{-1}, respectively. The water applied by the sprinkler was 0.51 cm day^{-1} for the first 3 months after fertilizer application and 0.56 cm day^{-1} for the next 2 months. Thus, for the shallower depths, the calculated water flux within the profiles was greater than the application rate. For the deeper depths and longer leaching time, the water flux within the profile was less than that applied due to increasing temperatures and greater evaporation. The overestimation of the water flux within the profile would result in an overestimation of the NO_3^- leaching also.

One explanation for the overestimation of the water flux within the soil is an overestimation of the soil-water velocity due to anion-exclusion or immobile water. Rolston and Marino (1976) determined for packed soil columns of Yolo soil with a similar water flux that approximately 8% of the water was not contributing to NO_3^- transport. However, if anion exclusion or immobile water was the reason for the overestimation of the water flux, a much larger portion of the water must not be contributing to NO_3^- transport in the field soil than that of laboratory columns in order to decrease the water flux sufficiently. The variability of NO_3^- concentrations at triplicate samplers of each depth also contributed to the uncertainty in determining the NO_3^- leaching component from flux of water and concentration of NO_3^-.

The recovery percentages of fertilizer N determined from concentration versus depth (Figure 38) was 50, 120, and 109% for the cropped, manure, and uncropped treatments, respectively. This approach more reasonably estimated leaching loss for these experiments than did estimations of water flux and concentration. Although this approach is not dependent upon knowledge of the water flux, it is plagued with averaging concentrations across any particular depth. Thus, it seems that anion exclusion, immobile water, or other unknown mechanisms may indeed be causing a considerable overestimation of the water flux and the resulting overestimation of the NO_3^- leaching in the field profiles.

Potential error in the leaching component from lateral movement of NO_3^- below the 60-cm deep barrier around each plot exists and would reduce NO_3^- recovery. This possible error was minimized by placing soil-solution samplers near the center of each 1-m^2 plot. This error does not appear to be very large in relation to the uncertainties in determining the water flux and the

TABLE 14. PERCENTAGE RECOVERY OF FERTILIZER N LEACHED IN THE h = -8 CM PLOTS OF THE WINTER EXPERIMENT CALCULATED BY VARIOUS WAYS OF DETERMINING THE SOIL-WATER VELOCITY. THE MEAN RECOVERY OF ALL DEPTHS FOR EACH PLOT IS GIVEN IN PARENTHESES

Method of determining pore-water velocity	% Recovery														
	Cropped					Manure					Uncropped				
	60	90	120	150	180	60	90	120	150	180	60	90	120	150	180
From v_s of each sampler	49	97	66 (62)	50	50	78	124	133 (128)	152	155	113	165	165 (167)	206	185
From mean v_s of all samplers at each depth (9 samples)	44	98	61 (56)	44	32	89	137	143 (138)	148	172	114	150	167 (182)	233	246
From mean v_s of all depths of one plot (15 samples)	50	103	67 (62)	51	40	83	120	131 (130)	142	176	107	132	154 (174)	225	253
From mean v_s of all depths of 3 plots (45 samples)	44	91	59 (55)	45	36	89	129	141 (140)	153	190	113	140	163 (184)	238	268

variability in NO_3^- concentrations at any particular depth.

Residual Soil N

The extractable soil N derived from the fertilizer as a function of soil depth for the h = -50 cm treatments of the low-temperature experiment is given in Figure 39. Extractable N for the h = -8 cm treatment was negligible.

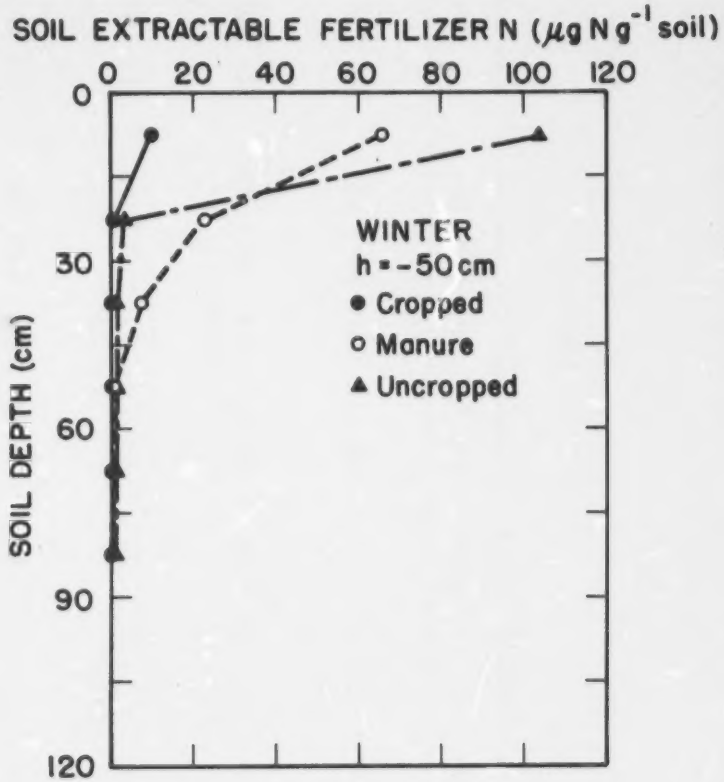

Figure 39. Soil extractable N from fertilizer as a function of soil depth, 4 months after fertilizer application in the winter experiment.

The data points are mean concentrations within 15-cm depth increments from eight samples. The extractable N in the h = -50 cm treatments was large in the upper 60 cm of soil due primarily to NO_3^- not yet leached from the upper portion of the profile.

The digestible soil N derived from the fertilizer as a function of soil depth for the six plots is given in Figure 40. As with the summer experiments, digestible soil N was greatest near the soil surface due to plant roots

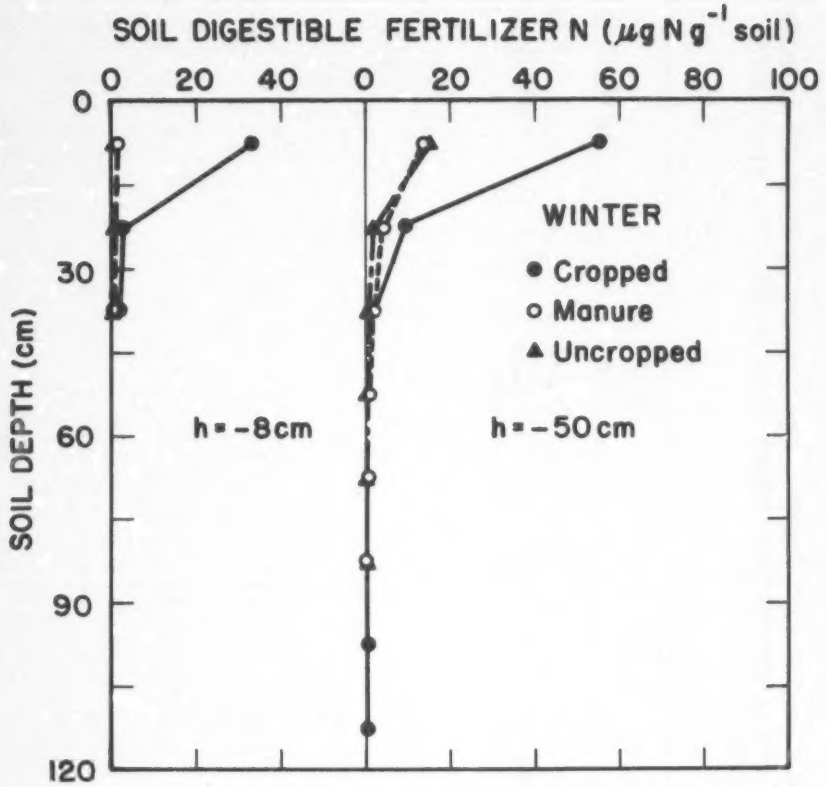

Figure 40. Soil digestible N from fertilizer as a function of soil depth, 4 months after fertilizer application in the winter experiment.

and microorganisms. The manure and uncropped plots had negligible plant growth, so the digestible N was primarily due to microbial immobilization of fertilizer NO_3^-.

Mass Balance

Table 15 gives the N balance for each of the components of the N cycle. Denitrification was determined by difference from fertilizer application, plant uptake, leaching and residual soil N. Denitrification was determined directly from N_2 and N_2O gas flux at the soil surface and any gaseous loss below the 60-cm barrier. The amount of fertilizer applied to each plot is given by Table 2.

The total denitrification as determined by the direct method was substantially less than that determined by difference in the h = -50 cm treatments. The direct method resulted in 41 to 64 kg N ha^{-1} less than that

TABLE 15. MASS BALANCE OF FERTILIZER N FOR THE WINTER EXPERIMENT. THE NUMBERS IN PARENTHESES WERE OBTAINED BY CALCULATING LEACHING FROM CONCENTRATION VERSUS SOIL DEPTH. THE MINUS SIGN INDICATES GREATER RECOVERY THAN FERTILIZER APPLIED

Treatment	Gaseous loss			Plant Uptake	Residual in soil		Denitrification	
	N_2O (kg N/ha)	N_2 (kg N/ha)	below 60 cm (kg N/ha)	Leaching (kg N/ha)	(kg N/ha)	Extractable (kg N/ha)	Digestible (kg N/ha)	Direct (kg N/ha)	Difference (kg N/ha)
Manure, h = -8 cm	4.2	27.1	1.5	406 (353)	---	0	3	33	(-62)
Manure, h = -50 cm	3.8	26.4	1.3	---	---	186	39	32	73
Cropped, h = -8 cm	0.7	17.6	0.5	168 (150)	118	0	70	19	(-38)
Cropped, h = -50 cm	0.1	1.9	0	---	137	22	71	2	66
Uncropped, h = -8 cm	0.4	0.0	0	535 (320)	---	0	2	0	(-28)
Uncropped, h = -50 cm	0.2	0.0	0	---	---	209	37	0	48

determined by difference after approximately 4 months. These differences are consistent with those measured in the summer experiment for the dry treatment and are explained by small rates of gaseous loss below the minimum detection limits for $^{15}N_2$. After 4 months, most of the NO_3^- remained in the upper 45 cm of soil in the h = -50 cm treatments. Temperatures gradually increased over the 4-month period. Thus, denitrification may have occurred at small rates since NO_3^- remained in the portion of the profile most conducive to anoxic development. The difference in denitrification between the direct and difference methods for the manure and cropped plots seems consistent with the difference observed in the summer experiment over comparable time periods of 4 to 5 months. However, the amount of denitrification as calculated by difference in the uncropped treatment is much greater than that determined in either of the uncropped plots of the summer experiment.

Although total denitrification of 48 kg N ha^{-1} in an uncropped plot maintained at h = -50 cm seems unrealistic compared with the results of the summer experiment, it has been shown that small changes in soil-air content, carbon level, and diffusion of oxygen through the soil surface can drastically change denitrification rates. A small change in the rate of denitrification occurring over several weeks can greatly increase total denitrification.

These results for the h = -50 cm treatments suggest that the sensitivity of the direct method of measuring the volatile denitrification products should be increased in order to measure small fluxes over long time periods. However, small fluxes over a long time may not be as important during normal irrigation or rainfall events due to generally rapid wetting and drying of the upper soil profile where most of the denitrification occurs. Research on rates of denitrification during and after irrigation cycles should provide further insight into the many interacting factors resulting in denitrification in field soils.

The comparison of denitrification by the direct and difference methods for the h = -8 cm treatments of the winter experiment was difficult due to recovery of much greater than 100% of the fertilizer by the difference method. This discrepancy was attributed to the inability to accurately measure leaching losses of NO_3^- from the soil profile. In addition to considerable variability in NO_3^- concentrations at individual depths, the determination of the soil-water flux was not sufficiently accurate to determine realistic amounts of leaching in any plot. Sampling variability of the residual soil N may also have attributed to failure in obtaining a mass balance. The most realistic method of determining the leaching component for the winter experiment was from concentration versus soil depth. Although this approach does not depend upon an accurate value for the soil-water flux, it does depend upon average concentrations at particular depths which may also be quite uncertain due to enormous spatial variability.

These results demonstrate the difficulty and potential uncertainty in determining denitrification by difference. Although uncertainties also exist for the direct determination of N_2O and $^{15}N_2$ flux from the soil surface, especially at small fluxes, rates and total denitrification are consistent and easily measured using ^{15}N fertilizer. The direct method is the only way that rates of denitrification from applied fertilizer can be practically measured.

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